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## ENHANCED BIORECLAMATION OF JET FUELS — A FULL-SCALE TEST AT EGLIN AFB FL

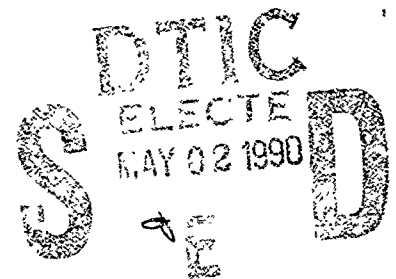
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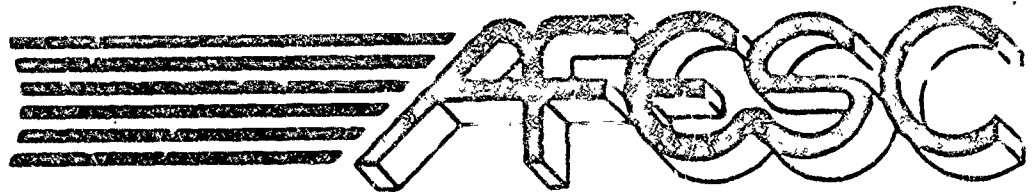
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<p>This report presents the results of a two-year, full-scale field test of enhanced biodegradation conducted at a JP-4 jet fuel spill site on Eglin AFB FL. A complete description of site characterization methods, the enhanced biodegradation process and hardware, and the impact of this technology on soil and ground water contaminants is provided. The report emphasizes the treatment limitations of this technology that were observed through intense monitoring of soil and ground water contaminant profiles. Significant problems with hydrogen peroxide decomposition were documented in this test. This rapid decomposition resulted in poor oxygen distribution and biodegradation rates which were far less than laboratory microcosm studies had predicted. Several recommendations for improving field applications of enhanced biodegradation are provided, including a checklist for performing pilot tests of this technology.</p>					
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## PREFACE


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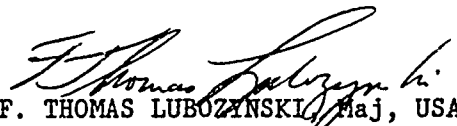
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This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

  
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## SECTION I

### INTRODUCTION

#### A. OBJECTIVE

The purpose of this full-scale test of enhanced in situ biodegradation was to determine the effectiveness of this technology for remediating JP-4 fuel spills. Because in situ biodegradation has the potential to destroy fuel contaminants without excavation or aboveground processing, it has enjoyed widespread public and regulatory attention. Despite growing commercialization of this technology, very little has been published on its limitations, its real costs, and its effectiveness in removing lower levels of contamination. This project was designed and monitored to answer these pressing questions and to provide recommendations to Air Force engineers considering the use of this technology.

#### B. BACKGROUND

##### 1. Problem Statement

Each year the U.S. Air Force stores and transfers billions of gallons of JP-4 jet fuel at over 200 Air Force installations. Fuel leaks and spills are by far the most frequent sources of soil and groundwater contamination on these installations. An estimated 1,500 fuel spills have been identified. That number could double as the Air Force begins to investigate its underground storage tanks. The Environics Division of the Air Force Engineering and Services Center (AFESC), located at Tyndall AFB, Florida, is responsible for developing and testing improved methods of soil and groundwater decontamination. Enhancing the natural biodegradation of fuel residuals is an emerging technology under investigation by Air Force researchers.

In 1984, AFESC initiated a pilot-scale test of enhanced biodegradation at a site on Kelly AFB, Texas. As this test progressed, problems with soil permeability were encountered, reducing the delivery of hydrogen peroxide and nutrients through injection wells. This reduction in permeability was attributed to both the natural silt and clay soils and the precipitation of calcium phosphates formed as injected phosphates reacted with calcium in the soil (Reference 1). Permeability problems reduced the delivery of oxygen, and consequently little biodegradation occurred. On the basis of these results, a second site with more favorable soil permeability was selected at Eglin AFB, Florida.

In April 1984, a leak had been found in an underground jet fuel pipeline at the Eglin AFB petroleum, oils, and lubricants (POL) area. A preliminary site characterization estimated that 30,000-45,000 gallons of JP-4 jet fuel had contaminated approximately 4,000 cubic yards of soil and shallow aquifer material (Reference 2). Follow-up sampling in August 1985 decreased that estimate to 20,000 gallons. A series of shallow, gravel-filled trenches were installed perpendicular to the direction of fuel movement, and skimmer pumps recovered over 7,000 gallons of free product. By early 1986, free product had been reduced to levels which were nonrecoverable, and use of the skimmer pumps was discontinued.

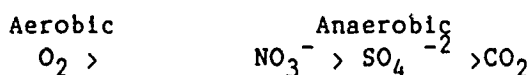
## 2. Fuel Degradation Pathways

Under favorable conditions, soil microorganisms will degrade most fuel hydrocarbon compounds. Controlled laboratory studies have demonstrated that a variety of indigenous soil microbes can aerobically degrade the mixture of aliphatic and aromatic compounds found in distillate fuels. Microorganisms that can degrade fuel components into carbon dioxide and water show greatest productivity in the presence of sufficient oxygen and inorganic nutrients such as nitrogen and phosphorus, a near-neutral pH, and warmer soil temperatures (Reference 3).

Anaerobic pathways are also available to degrade fuels, but their rates have been generally considered too slow to constitute an active cleanup. Anaerobic biodegradation of fuel hydrocarbons does occur, and has recently been documented both in field and laboratory research, (Reference 4; Reference 5; Reference 6; Reference 7; Reference 8; Reference 9), generally at lower rates and with somewhat less predictability than aerobic biodegradation (Reference 10).

Laboratory and field evidence suggests that microbial populations can use minute amounts of oxygen to initiate hydrocarbon oxidation, and that subsequent oxidation is sustained by alternative electron acceptors, such as nitrate or sulfate. Swain et al. (Reference 11) reported that the bacterium *Pseudomonas aeruginosa* degrades octane both aerobically and by denitrification if trace amounts of oxygen (<0.05 mg/L) are present. If oxygen was entirely excluded, however, degradation did not proceed. Kuznetsova and Gorlenko (Reference 12) reported that aerobic *Pseudomonas* initially attacks hydrocarbons at the upper edges of rims of oil fields, and that the partially oxidized products of this process are further oxidized by sulfate reducers, with concomitant formation of  $H_2S$ .

Electron acceptors are generally used preferentially in the order:



Thus, oxygen is preferred over nitrate, nitrate over sulfate, and sulfate over carbon dioxide (methane fermentation). The reduced products of these electron acceptors are water, nitrogen gas, hydrogen sulfide, and methane, respectively.

The introduction of nitrate as the terminal electron acceptor to the subsurface is being studied as an alternative oxidant delivery method which could use denitrifying organisms to assist the degradation process. Field demonstrations of this technology have been conducted in Germany (Reference 4) and in Canada (Reference 13). In both cases, nitrates were actually added to groundwater to stimulate anaerobic denitrification, resulting in accelerated fuel degradation. To the authors' knowledge, in the United States only one relatively undocumented attempt at nitrate utilization has been reported (Reference 14). The nitrate process is currently being field-demonstrated by the EPA at a site in Michigan. Perhaps because of regulatory difficulties and potential permitting and liability problems associated with injection of nitrates into groundwater, the process is not widely practiced in the U.S.

### 3. Enhanced Bioreclamation

Enhanced bioreclamation, as typically applied, is an engineered system which creates favorable conditions for accelerated aerobic biodegradation. The most commonly used oxygen source in the United States is oxygen injected in the form of hydrogen peroxide ( $H_2O_2$ ). The hydrogen peroxide breaks down into oxygen and water. Using hydrogen peroxide, it is theoretically possible to inject available oxygen at levels far above oxygen's solubility. The chief problems encountered in field application are typically associated with nonhomogeneous soils, complex geochemical balances, and a moving fuel target. Under these conditions, scale-up from laboratory tests is difficult. The success of aerobically enhanced bioreclamation depends primarily on the contact of sufficient oxygen with fuels contained in both the groundwater and the soils. This contact depends on the distributions of  $H_2O_2$  and the control of its decomposition into oxygen. Table 1 emphasizes the importance of oxygen delivery and soil permeability to the process. The state of the art for this technology is largely defined by the methods used to achieve oxygen contact.

The EPA Handbook on Remedial Action at Waste Disposal Sites (Reference 15) contains an overview of enhanced bioreclamation and summarizes much of the available data on past site demonstrations. To the authors' knowledge, only the nitrate demonstrations previously discussed have been attempted to clean up fuel hydrocarbons anaerobically. For this reason, the remainder of the discussion will focus on fully aerobic enhanced bioreclamation. Although the general methods of enhanced in situ bioreclamation are described in the open literature, information on the methods of oxygen delivery and hydrogen peroxide stabilization has been largely protected by proprietary interests. Likewise, data are seldom available on the level of treatment achieved by enhanced biodegradation in reducing groundwater-soluble fuel components and soil residuals to ug/L and ug/kg levels.

### 4. Physical Factors

The specific physical and chemical properties of soils and groundwater, and the location of hydrocarbons in relation to the water table, are often the deciding factors in the application of this technology. Free product (free product refers to the free-phase floating fuel) is generally removed before full-scale injection of the nutrients and oxygen begins. Complete removal of all free product cannot be easily achieved. In practice all "recoverable product" is removed, typically leaving intermittently observed thin layers or sheens of product. These small amounts of free product remaining at the groundwater interface are distributed in the soils or washed out as water is circulated through the site. The intermittent occurrence of free product may increase the difficulty of monitoring the progress enhanced biodegradation.

Successful bioreclamation depends on maximum contact between the enriched injection water, the microorganisms, and the fuels; however, the majority of fuel at most sites is sorbed or occluded within soil particles and not dissolved in groundwater. Low hydraulic conductivity of clay or layered soils and reduced permeability due to chemical precipitation presents a major obstacle to enhanced biodegradation, as was demonstrated at a pilot demonstration at Kelly AFB, Texas (Reference 1). A similar problem is encountered at

TABLE 1. MINIMUM PUMPING REQUIREMENTS FOR AEROBIC ENHANCED BIODEGRADATION

Oxidant Injection	Air Saturated Water	Oxygen Saturated Water	100 mg/L Peroxide	300 mg/L Peroxide	500 mg/L Peroxide
Available oxygen	10 mg/L	40 mg/L	50	150	250
Minimum volume of water (gallons) required to remediate 1,000 gallons of fuel	290,000,000	58,000,000	46,000,000	15,000,000	10,000,000
Theoretical minimum pumping time (years) required <sup>a</sup> to treat 1,000 gallons of fuel					
Gravel ( $k=10^4$ gal/day/ft <sup>2</sup> )	0.4	0.08	0.063	0.02	0.014
Sand ( $k=10^2$ gal/day/ft <sup>2</sup> )	40	8.0	6.3	2.0	1.4
Silt ( $k=1$ gal/day/ft <sup>2</sup> )	4,000	800	630	200	140
Clay ( $k=10^{-3}$ gal/day/ft <sup>2</sup> )	4,000,000	800,000	630,000	200,000	140,000

<sup>a</sup> Assumes treatment area 100 x 100 feet with an average induced gradient of 0.2 (20 feet of differential across the site).

sites with limited groundwater yield, particularly when much of the contamination resides in the unsaturated zone. As illustrated by Table 1, a large volume of water is needed to deliver oxygen to fuel residuals. For this reason, enhanced bioreclamation is best suited to permeable soils where the bulk of the fuel contamination resides at or near the groundwater interface. To the authors' knowledge, enhanced bioreclamation is the only demonstrated technology for in situ treatment of hydrocarbons in deeper groundwaters.

## 5. Chemical Factors

Soil and groundwater chemistry are also important when evaluating a site for enhanced bioreclamation. The pH and oxidation-reduction balance of groundwater is complex and sensitive to the introduction of oxygen and other chemical species. Hydrogen peroxide, sodium salts, ammonia, and phosphates, all of which are used in nutrient solutions, can react with ferrous and ferric iron, manganese, calcium, and other ions. Of greatest concern are reactions that destabilize hydrogen peroxide or those that form precipitates which reduce permeability and groundwater flow. While it is not clear whether or not the presence of iron and other ions precludes the use of hydrogen peroxide for enhanced bioreclamation, iron removal systems and/or the addition of phosphates to preserve hydrogen peroxide stability or chelators to form non-reactive complexes with the metallic ions may be required. It is not clear that such measures can sufficiently improve hydrogen peroxide stability to ensure the success of enhanced bioreclamation. In these situations, alternatives to hydrogen peroxide, such as nitrates or other oxygen sources, may be considered.

Measuring the progress and final impact of enhanced bioreclamation is a difficult task of great importance. While the available literature on site demonstrations has reported some data on hydrocarbon reduction in groundwater and increases in microbial populations, little information is available on total hydrocarbon reductions in soils (Reference 15). Critics of enhanced bioreclamation often point out that dilution or drawdown of water to a level below the contaminated soils accounts for much of the reported reductions in groundwater contamination. Intense sampling of soils and groundwater, before and after treatment, is necessary, including laboratory analysis for benzene, toluene, and xylenes and/or other appropriate individual less-soluble fuel fractions. It should be noted that benzene, toluene, and xylenes typically make up only a small fraction of any fuel, and as they are among the most soluble components their behavior should not be considered indicative of the behavior of other petroleum hydrocarbons. Care must be taken to ensure that a complete hydrocarbon mass balance is achieved and that observed decreases are not due simply to dilution, redistribution of fuels in the soil profile, sampling variability, or bias.

## C. SCOPE

Following a review of over 50 JP-4 fuel spill sites, the Eglin AFB site was selected for this full-scale technology demonstration. The test was divided into several important subtasks which progressed from bench-scale biodegradation studies to the evaluation of full-scale operating systems and their impact upon the 4,000 cubic yards of hydrocarbon contaminated soil and shallow groundwater.

Initial soil and groundwater samples were analyzed for JP-4 jet fuel contaminants, microbial populations, and nutrient availability. Laboratory treatability studies were used to analyze the response of microorganisms to increased oxygen and nutrient levels and the ability of microbes to degrade fuel under enhanced conditions. Laboratory studies on nutrient transport and hydrogen peroxide stability were also completed prior to full-scale design.

A system for delivering nutrients and oxygen (in the form of hydrogen peroxide) to the subsurface was designed. Three application methods were established for side-by-side testing: injection wells, infiltration galleries, and spray infiltration. Four recovery wells were installed and pump tests performed to determine the hydraulic capacity of the site. Following approval of the test plan by the Florida Department of Environmental Regulation (FDER) the application system was constructed and put into operation in March 1987.

Over an 18-month period, approximately 7,800 pounds of inorganic nutrients and 94,000 pounds of 35 percent hydrogen peroxide were injected into the subsurface. Problems with hydrogen peroxide stability were encountered which reduced the delivery of oxygen to microbes in the subsurface. This report summarizes the important observations on the applicability and effectiveness of enhanced biodegradation in removing fuel contaminants from soil and groundwater.

## SECTION II

### SITE CHARACTERIZATION STUDIES

On the basis of available information, a site characterization in support of an enhanced biodegradation demonstration was designed and initiated in 1986. A step-wise approach to this investigation was taken:

- . review the results of previous investigations
- . conduct an initial soil gas survey to determine the extent of highly contaminated soils and groundwater
- . construct monitoring wells to verify the result of the soil gas survey and permit collection of groundwater samples for analysis
- . collect soil samples in locations corresponding to monitoring wells
- . carry out pump tests to determine hydraulic characteristics of the aquifer.

A brief summary of initial site conditions is provided here; the details of this study can be found in subsequent sections.

The results of the initial soil gas survey are illustrated in Figure 1. The 1-ppm benzene and toluene isopleths agree well with past observations of the maximum extent of free product. This was interpreted to indicate that the area within the 1-ppm isopleths, in which free product had been observed in the past, was where the highly contaminated soils and groundwater could be found.

Tables 2 and 3 indicate the estimated JP-4 contaminant mass and typical concentrations observed in the highly contaminated area at the initiation of this study. Figure 2 illustrates the distribution of Total Petroleum Hydrocarbons in soils across the site. As can be seen, the bulk of the contamination was found in the vadose zone. The site soils were generally sandy, with low levels of naturally occurring organic nutrients. Table 4 illustrates the total iron and calcium content of the soils above and below the water table from a typical location.

#### A. SITE SETTING

##### 1. Location, Physiography, and Topography

Eglin Air Force Base is located in southern Okaloosa County, in the panhandle of northwest Florida near the city of Valparaiso. The main portion of the base is situated six miles north of Fort Walton Beach and the Gulf of Mexico. Past and current investigations have focused on a 5-acre parcel of the base's fuel storage facility between Eighth Street, Eglin Boulevard, the Eglin AFB athletic fields (including Foster Stadium), and Weekly Bayou. A portion of this area was chosen as the enhanced bioreclamation demonstration site.

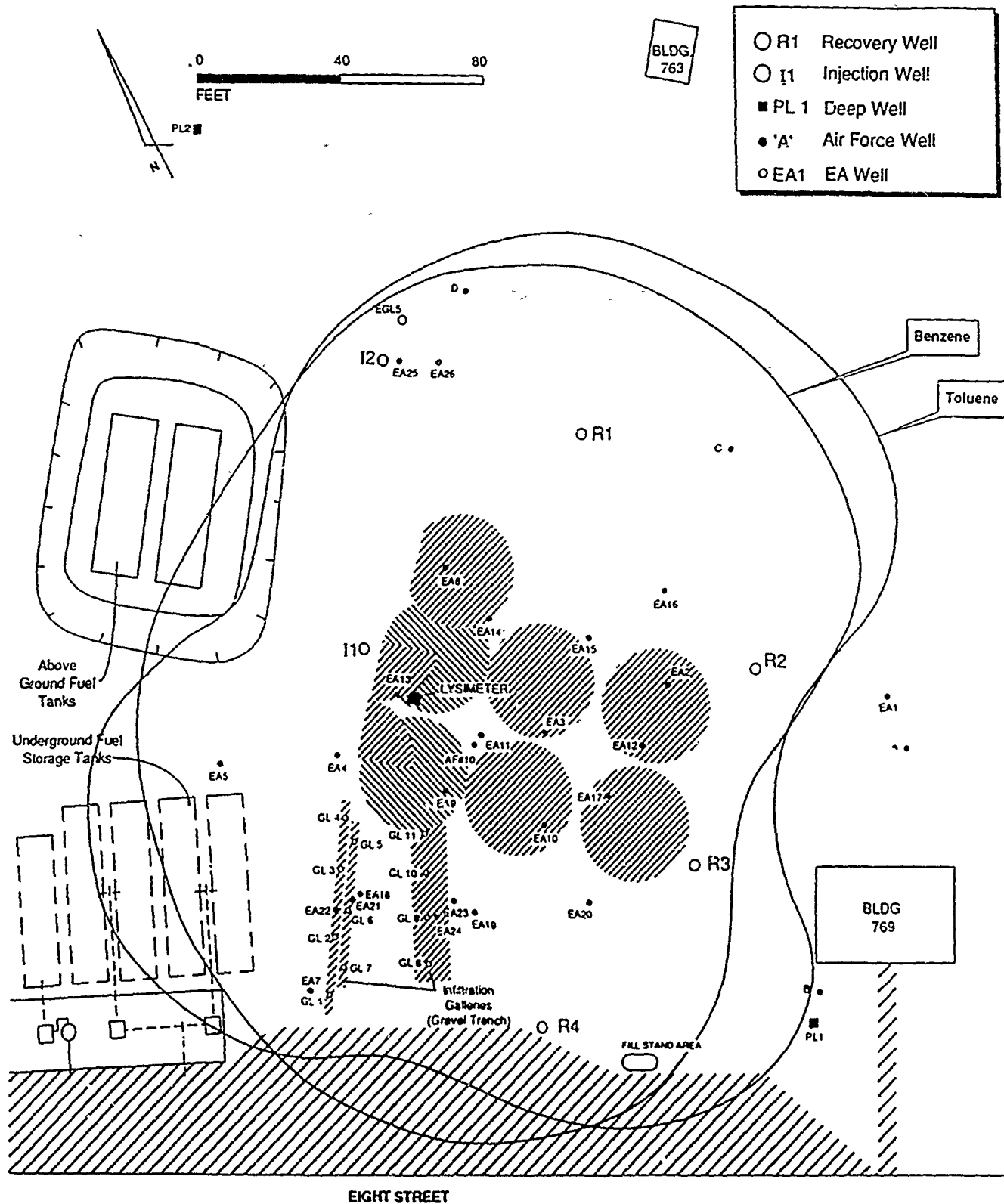


Figure 1. Locations of Soil Vapor Collection Points and 1:1 Benzene/Toluene Isopleth, Eglin AFB, Florida, November 1986.

TABLE 2. ESTIMATED MASS BALANCE OF UNDERGROUND HYDROCARBONS  
AT THE POL AREA, EGLIN AFB, NOVEMBER 1986

Description	Volume (gal)	Mass (lb)	Reference
Spill at time of discovery (27 April 1984)	35,000 (30,000- 40,000)	219,000 (188,000- 250,000)	30-45,000 est. (Weston 1984)
	20,000	125,000	(Geraghty & Miller 1985)
Fuel recovered by September 1984	7,400	46,270	(Weston 1984)
Amount remaining November 1986	2,650	16,500	Estimated, this study
Unsaturated zone	(2,600)	(16,200)	
Saturated zone	(50)	(300)	
Unaccounted-for <sup>a</sup> loss	9,900	62,000	

<sup>a</sup> Possibly lost through overland flow during storms and/or by volatilization; estimated on basis of 20,000-gal initial spill estimate.

Assumptions: dimensions of contaminated (water-) saturated, region 25,000 sq ft x 2.5 ft.; total petroleum hydrocarbon concentration in saturated region, 200 mg/L; dimensions of contaminated unsaturated region 25,000 sq ft x 2.5 ft.; total petroleum hydrocarbon concentration in unsaturated region, 2,000 mg/kg; porosity = 0.35, specific gravity of hydrocarbons = 0.75.

TABLE 3. INITIAL SITE CONDITIONS IN CONTAMINATED AREA<sup>a</sup>  
AT THE EGLIN POL DEMONSTRATION SITE

Parameter	Soil (Mg/kg)	Groundwater (Mg/L)
TOC	-	126 (18)
TPH	2000 (20)	-
BTX <sup>b</sup>	110	6
C <sub>8</sub> - C <sub>17</sub> <sup>c</sup>	640	3
PO <sub>4</sub>	-	<0.2
NH <sub>4</sub>	-	8
Fe (total)	-	12 (<0.5)
pH	-	5.4 units (6)
Dissolved O <sub>2</sub>	-	<1 (3)
Temperature	-	20 C
Total Bacteria (10 <sup>5</sup> CFU)	2	15
HC Degradars (10 <sup>5</sup> CFU)	0.9	1.6

<sup>a</sup> Average of contaminated monitoring locations

<sup>b</sup> Total benzene, toluene and xylenes

<sup>c</sup> Total alkanes detected by GC/MS

( ) = Uncontaminated background level

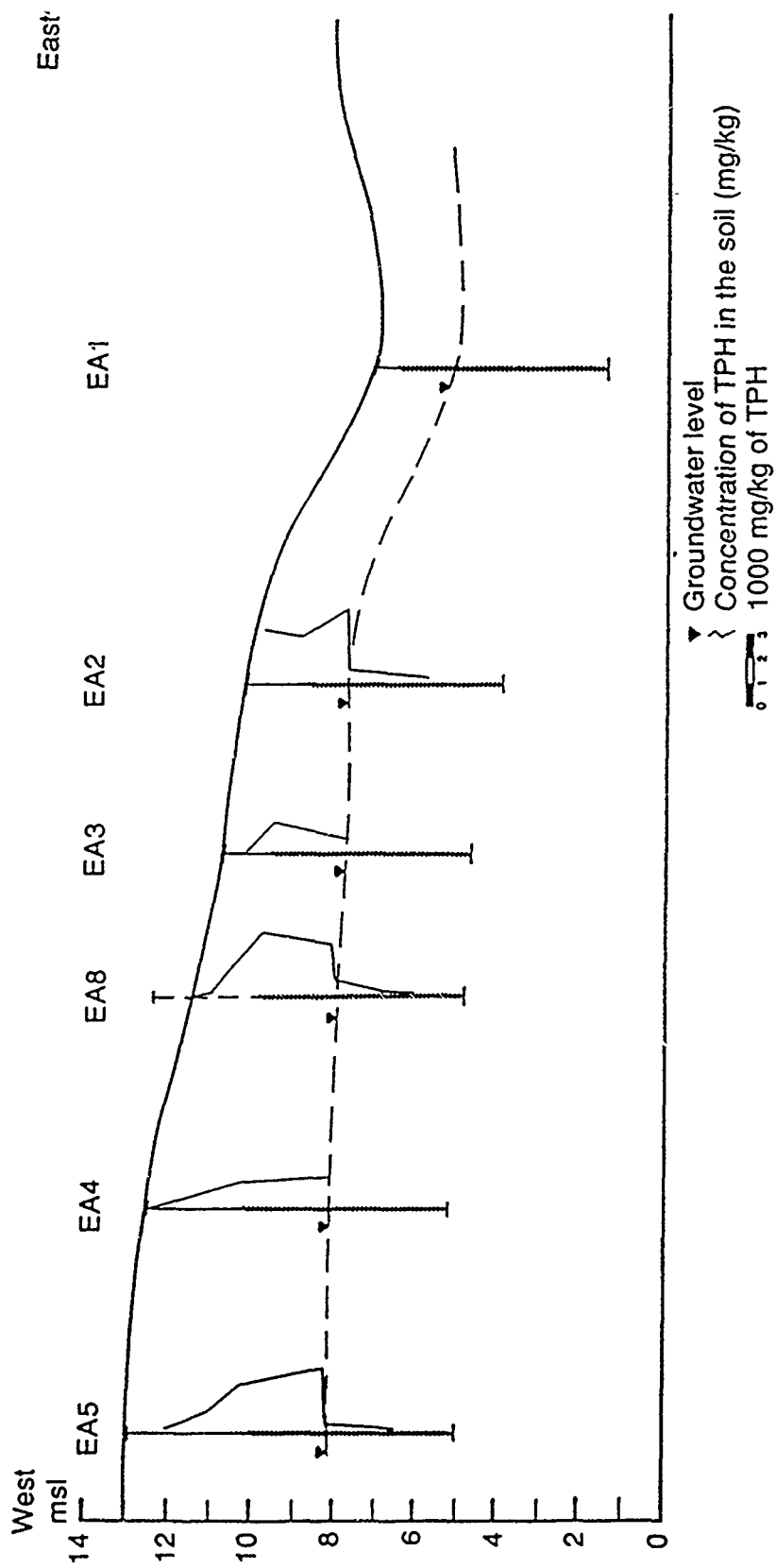


Figure 2. Surface and Groundwater Levels, Well Profiles, and Distribution with Depth of Total Petroleum Hydrocarbons (TPH) at the Eglin POL Demonstration site.

TABLE 4.. IRON AND CALCIUM CONTENT OF SOILS COLLECTED FROM  
THE VICINITY OF EA-8 AT THE EGLIN POL DEMONSTRATION  
SITE (mg/kg)

<u>Sample Depth Below Surface (feet)</u>	<u>Calcium</u>	<u>Iron</u>	<u>Hydraulic Condition</u>
1	1.8	590	Unsaturated
2	0.77	400	Unsaturated
3	1.1	500	Unsaturated
4	0.45	25	Saturated
5	0.48	25	Saturated
6	0.56	32	Saturated
7	0.35	37	Saturated

Eglin Air Force Base is located in two physiographic provinces that characterize northwestern Florida: the Bay Sinks of the Western Highlands, formed as permeable materials locally filled depressions in otherwise impermeable rocks (Reference 16), and the sand dunes, beach ridges, and wave-cut bluffs constitute the Coastal Lowlands (Reference 16) or Gulf Coastal Lowlands (Reference 17). The demonstration site lies within the Coastal Lowlands. Physiographic provinces are generally determined by the type of surficial sediments found in each division and surficial sediments greatly affect groundwater systems. The sand dunes and beach ridges of the Coastal Lowlands in which the demonstration site is located are well-drained. The water table is directly related to topography, being a subdued historical replica of the topography a few feet below the land surface (Reference 17).

The topography of northwest Florida was created by the deposition and erosion of sediments by oceans, rivers, and streams as the sea level fluctuated. The land surface at the demonstration site slopes down to the northeast toward Weekly Bayou, ranging in elevation from 12 feet near building 769 to sea level at the bayou, 550 feet to the east and northeast. Surface water drainage culverts convey storm run-off under roadways to downgradient discharge points. Weekly Bayou is the nearest body of standing water.

Okaloosa County has a humid, subtropical climate (Reference 18). Summers are warm (average temperature 82°F), and winters are mild (average temperature 50°F), with few frosts from November through February. Annual rainfall measured at the National Weather Service station in Niceville has ranged from 31 inches, in 1954, to 95 inches, in 1975; the mean rainfall was 64 inches (Reference 18). Rainfall is consistent in the winter months, December through April. Strong, localized showers produce the highest accumulations in the summer months. Rainfall is the main source of recharge to the groundwater systems in the area.

## 2. Site Stratigraphy and Geology

Approximately 1,500 feet of coastal plain sediments, ranging in age from middle Eocene to Holocene, make up the system of aquifers and confining beds in Okaloosa County. These sediments are predominantly clastic sand, clay, and limestone. In general, the strata dip to the southwest at 15 to 20 feet per mile. Barr and others have correlated seven stratigraphic units with six hydrogeologic units (Table 5).

## 3. Hydrogeology

In descending order (shallowest to deepest), the principal hydrogeologic units of Okaloosa County are shown in Table 5.

The Sand-and-Gravel Aquifer crops out through Okaloosa County and at the Eglin POL demonstration site. It consists predominantly of very-fine-to-coarse quartz sand. Gravel and clay are scattered as isolated lenses and stringers: the gravel lenses consist of 10-75 percent small quartz pebbles. Grains of quartz are coated with pale colored clays. Limonite is found in thin beds and accumulations. The Sand-and-Gravel Aquifer dips south-southwest at a rate of 15 to 25 feet per mile and thickens generally east to west from

TABLE 5. STRATIGRAPHIC AND HYDROGEOLOGIC EQUIVALENTS  
OF SOILS UNDERLYING EGLIN AFB, FLORIDA

<u>Stratigraphic Unit</u>	<u>Age</u>	<u>Hydrogeologic Unit</u>
Unnamed Holocene-to-Pliocene sands and Citronelle Formation, undifferentiated	Holocene-to-Pliocene	Sand-and-gravel aquifer
Miocene coarse clastics Intracoastal Formation Alum Bluff Group Pensacola Clay	Miocene	Pensacola Clay confining unit
Bruce Creek Limestone	Miocene	Upper Limestone
Tampa Limestone equivalent and undifferentiated Limestone,	Oligocene	Upper Limestone of the Floridan Aquifer
Bucatanua Formation	Oligocene	Bucatanua clay confining bed
Ocala Limestone	Eocene	Lower limestone of the Floridan Aquifer
Lisbon and Tallahata Formations	Eocene	Lisbon-Tallahata confining unit

20 to 40 feet: it is approximately 40 feet thick at the demonstration area. In well PL-2 at the demonstration site, the underlying Pensacola Clay was intersected at 43 feet (Reference 19).

The thickness and relative impermeability of the Pensacola Clay generally allows it to serve as an aquitard to the Sand-and-Gravel Aquifer and an upper confining bed to the Floridan aquifer. Where present, as it is in Okaloosa County, the Pensacola Clay restricts vertical movement of water between the Sand-and-Gravel Aquifer and the Floridan Aquifer. The Pensacola Clay contains very dense clay with some clayey sand, coarse, angular gravel, limestone, and shell fragments. It is between 50 and 475 feet thick, beginning at depths of 10 to 210 feet, and it dips to the southwest 15 feet per mile. A vertical conductivity of  $4.9 \times 10^{-7}$  feet per day was calculated in Milton County (Reference 17), but conductivity averages  $1 \times 10^{-5}$  feet per day in Okaloosa County (Reference 18). At the demonstration area, (Reference 19) measured a permeability of  $2.3 \times 10^{-8}$  cm/sec ( $1 \times 10^{-4}$  feet per day) in a sample of the clay.

Below the Pensacola Clay lies the Floridan Aquifer. The Floridan Aquifer is divided into two hydraulically isolated units by the relatively impermeable Bucatunna Clay member of the Byram formation. Carbonate rocks constitute the major portion of the Floridan aquifer, but locally the carbonate rocks grade into coarse sandy gravel. The upper Oligocene member and the lower Eocene member together are more than 1,000 feet thick. The surface of the Floridan aquifer dips to the southwest at 20-35 feet per mile. The Gulf of Mexico sedimentary basin is responsible for this southwest dip. Interconnected intergranular spaces and fissures in the upper limestone member are the principal source of water in southwest Florida: the locally fossiliferous lower member contains saline water, especially in coastal areas, rendering it useless as a source of water.

The Bucatunna Clay confining unit that separates the Floridan aquifer into two units consists of relatively low-permeability material like clay or sandy clay. The Bucatunna Clay is present only in the southern part of Okaloosa County: to the north, the Floridan Aquifer occurs as a single unit. The top of the Bucatunna dips south-southwest at 25 feet per mile, at depths of 700-1,000 feet below sea level.

The Lisbon-Tallahata unit acts as the lower confining unit for the Floridan Aquifer. It is composed of gray shale-like limestone, very-fine-to-coarse-grained sand, and gray-to-brown clay. The top of the Lisbon-Tallahata confining unit ranges in depth from 900 to 1,300 feet from the surface. It dips 12-16 feet per mile to the south-southwest (Reference 18).

The report of Geraghty and Miller (Reference 19) indicated that the JP-4 contamination at the demonstration site was limited to the upper Sand-and-Gravel Aquifer. As most water supply wells in this part of Florida are completed below the Pensacola clay, risk to these wells could only occur if contaminants were to migrate downward through the clay. Geraghty and Miller concluded that this was very improbable. There appear to be no water supply wells impacted by this contamination plume. It is anticipated that the plume will eventually discharge into Weekly Bayou. The site was selected for research partly because of its low risk to human populations and aquatic ecosystems.

## B. PREVIOUS SITE CHARACTERIZATION

Prior to initiation of the current project, site investigations were conducted by the Air Force, both directly and through contractors.

1. U.S. Air Force Study. Figure 3 shows the locations of key monitoring wells used in these studies. The term "U.S. Air Force" describes investigations conducted wholly in-house by USAF personnel. Air Force personnel, recognizing that local vegetation was being damaged by a possible fuel spill and/or pipeline leak, reported the spill to the Florida Department of Environmental Regulation (DER) and the Environmental Protection Agency. Trenches were constructed around the suspected contaminant plume to determine the approximate extent of the spill. A hand auger was used to probe depths to groundwater and free product. Twelve of these borings were converted to monitoring wells by installing 4-inch diameter PVC screened casings. These wells have been sampled and the samples analyzed at regular intervals. The deepest wells were 10 feet deep, but most were 5 to 6 feet deep. The Air Force continued monitoring selected wells on a periodic basis.

2. Roy F. Weston, Inc. Study. Roy F. Weston, Inc. was retained by the Air Force in 1984 to identify the source of contamination, to delineate the horizontal extent of the contaminant plume, and to suggest a long-term plan of recovery and remediation (Reference 2). The fuel in the ground was identified as JP-4 jet fuel containing aromatic contaminants, including benzene, toluene, and xylenes. The spill was estimated at 30,000-40,000 gallons. Storage tanks and transfer lines were leak-tested with water at 175 psi. A leak of 1/3 gallon per minute at 45 psi in an unused stub of a steel transfer line was found in the vicinity of EA-5; another significant leak was located in delaminated fiberglass piping near Tank T-28. Two other, minor leaks were located in transfer lines.

To investigate floating fuel and groundwater flow, 71 monitor points were set with a hand auger to begin groundwater monitoring. The monitoring network permitted the collection of hydrogeological, physical, and chemical data for the site. The plume was found to extend to within 390 feet of Weekly Bayou. Weston's work suggested that because of the low hydraulic gradient, the plume was moving slowly to the northeast toward Weekly Bayou, at a rate of 40 feet per year. Maps of the elevations of fluid surfaces were constructed. The plume remained rather stationary for four months after the original discovery. Weston (Reference 2) estimated that the plume could introduce 0.08 gallons of JP-4 per day to Weekly Bayou, assuming no natural biodegradation or volatilization occurs.

Weston recommended a passive long-term program of intermittent pumping of free-floating fuel without deliberate stressing of the aquifer. An interim recovery system consisting of gravel-filled recovery trenches, interceptors, transfer lines, gravity separation, and storage for collected fuel was installed. By October 1984, an estimated 7,400 gallons of fuel had been collected (Reference 2).

3. Geraghty and Miller Study. The firm of Geraghty and Miller was issued a contract in 1985 (Reference 19) to assess the environmental impact of the contamination on the surrounding plant and animal environments and to conduct a further assessment. In this assessment, the toxicity of the aromatic

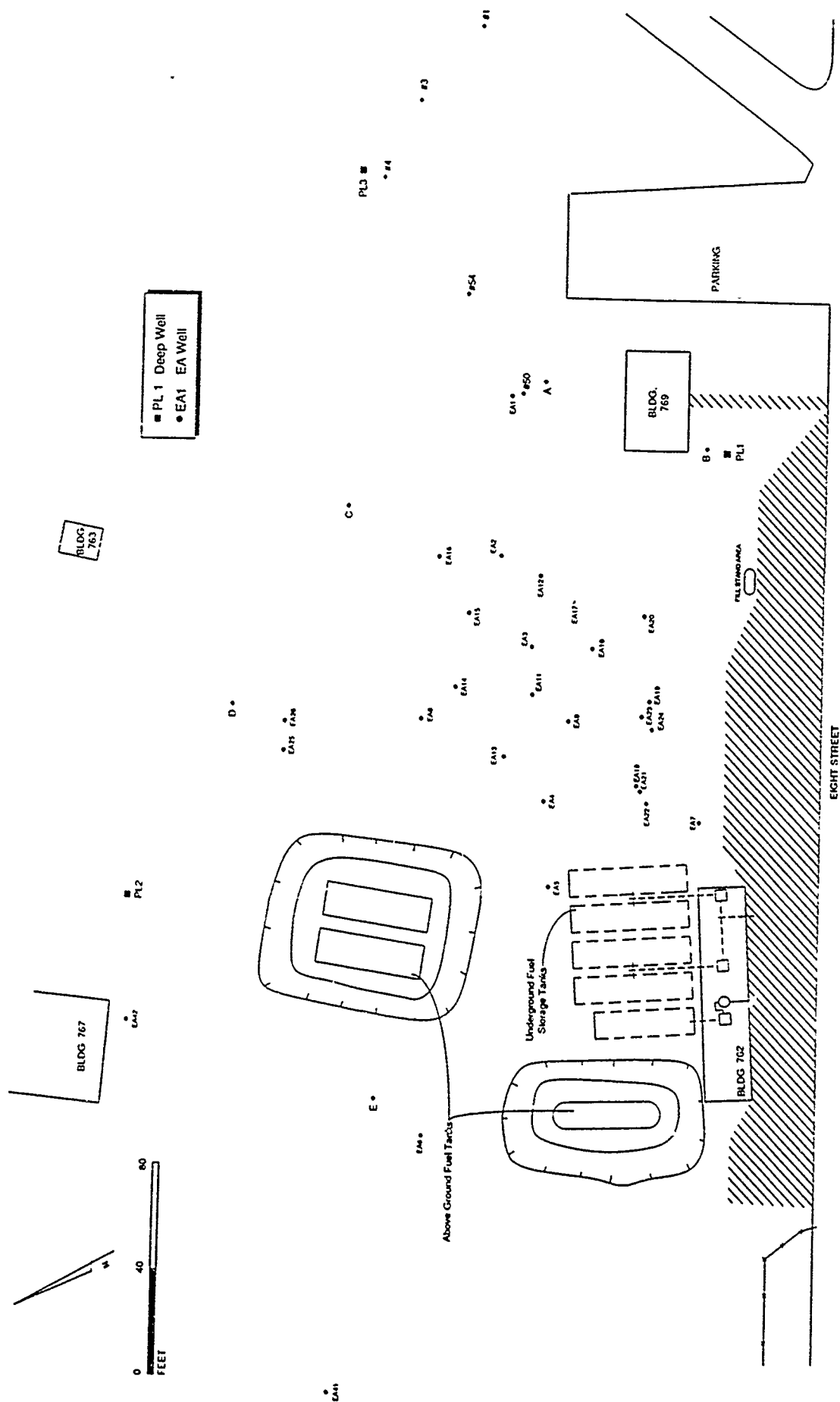


Figure 3. Locations of Monitoring Wells at the Eglin POL Demonstration Site.

components was reviewed. Three deep (45-50 foot) monitoring wells (PL-1, PL-2, and PL-3) and five shallow monitoring wells (A, B, C, D, and E) were installed and contributed to delineation of the vertical extent of the contaminant plume. The wells were constructed with 2-inch diameter PVC screened casing in a 6-inch diameter hole that had been packed with gravel; the upper annulus of each well was neat grouted. Geraghty and Miller suggested that the vertical extent of the plume was limited, because vertical movement is restricted by the Pensacola Clay confining unit. Geraghty and Miller measured a permeability of 0.0212 cm/sec and 0.0188 cm/sec for sands of the Sand and Gravel Aquifer with a falling head laboratory method. A permeability of  $2.3 \times 10^{-8}$  cm/sec was measured by a similar method for silty clay (Pensacola Clay) taken from a depth of 48-50 feet in PL-2. A hydraulic gradient of 0.015 ft/ft and a saturated thickness of 40 feet were estimated for the Sand and Gravel Aquifer.

### C. PRESENT INVESTIGATION: FIELD SAMPLING METHODS

#### 1. Soil Gas Analysis

Soil gas samples were collected for hydrocarbon vapor, oxygen, and carbon dioxide analysis. Soil gas samples were collected by driving 5/8-inch-diameter stainless steel probes to a depth of 2 feet below the surface of the ground. A suction pump was used to purge gas from the probe and draw gas from the soil. The gas was collected with a syringe and injected for hydrocarbon analysis into a portable gas chromatograph (Photovac 10S50) that was calibrated to quantitatively measure benzene and toluene. Carbon dioxide was quantified utilizing Draeger tubes. Oxygen was quantified with a Gas Tech explosimeter.

#### 2. Soil Sampling

Soil samples were collected from the unsaturated zone by hand-excavating to the appropriate depth. Soil samples were collected from below the water table with a hand-driven split-spoon sampler. Soil samples to be analyzed for organics by gas chromatography/mass spectrometry (GC/MS) were quickly placed into 40-mL glass vials with Teflon<sup>R</sup> caps. Soil samples for TPH and other analyses were placed in 350-mL soil jars. All samples were stored and shipped on ice to the laboratory. All sampling and sample handling was done under chain of custody procedures.

#### 3. Groundwater Sampling

##### a. Monitoring Well Construction

Because of the very shallow groundwater conditions and the easily worked sandy soils, all monitoring wells identified as "EA" wells were installed by hand. The locations of these wells are shown in Figure 3. Installation was accomplished digging to the water table, then jetting the well to the desired depth. All EA monitoring wells were constructed of 2-inch PVC with 5 feet of 0.02-inch screen and 2-5 feet of blank casing above, and all wells were fitted with end caps. EA monitoring wells were installed with a screen depth 3 feet below the water table. Two feet of

screen was left above the water table to allow for changes in water elevation. The other wells sampled in the project, B and D, were of unknown construction.

#### b. Sampling Procedures

Before sample acquisition, wells were purged to ensure that the sample collected was as representative as possible of the groundwater in the aquifer. Purging was accomplished by using a bottom-filling bailer. Each well was purged of a volume of water equal to four or more times the volume of standing water in the casing. Frequently, before bailer purging, wells were prepurged with a 1-gpm suction pump for 15-30 minutes.

Groundwater was sampled with bottom-filling Teflon<sup>R</sup> bailers. Only sampling gear that had been properly cleaned was used. Prior to sampling, wells containing free product were bailed to a product thickness of 1/4 inch or less: the samples were then taken in a manner which minimized the introduction of free-product JP-4 into the samples. A new, clean, dedicated piece of noncontaminating line was attached to the bailer for each well. Care was exercised to ensure that the bailer and line did not contact the ground or other sources of contamination. The bailer was lowered into the well until it filled, then it was retrieved and the water was discarded. This process was repeated three times. The bailer was then filled and the sample was transferred to the sample containers. Samples for volatile organics were collected in a manner that minimized aeration, and the containers were closed free of bubbles and headspace. After the containers were filled, they were labeled, an entry was made on the chain-of-custody form, and they were placed in a cooler on ice. All samples were shipped to the laboratory by Federal Express. To further reduce the possibility of cross-contamination, the wells were sampled so that the least-contaminated wells were sampled first.

#### c. Well Gauging

Water levels were measured with a Marine Moisture Corporation (MMC) oil/water interface probe. Upon arrival at each well, the following protocol was followed: first the height of the stick up was measured. This reference was checked to ensure that the well had not been altered. The depth to product, depth to water, and, at times, the depth to the bottom of the well were then measured. The MMC oil/water interface probe operates on the principle of sonic conductivity: the MMC probe produces an audible signal when immersed in liquid. The signal is continuous when the probe is immersed in material less dense, and less sonically conductive, than water (e.g., JP-4) and is intermittent when immersed in water.

### D. METHODS OF ANALYSIS

#### 1. Field Analysis

Field analytical techniques (other than those used in conjunction with the soil gas survey described in Section II.A.3) were utilized to determine the concentrations of the following parameters in the groundwater:

Oxygen  
Temperature  
pH  
Hydrogen peroxide  
Chloride  
Orthophosphate  
Ammonia nitrogen

Oxygen and pH were determined using portable field instruments. When oxygen concentrations exceeded the instrument's 20 mg/L limit, the water sample was diluted in a 1:1 ratio (or greater as necessary) with oxygen-free water which was prepared by vigorously purging tap water with nitrogen. Groundwater temperature was also noted.

Field test kits were used to determine hydrogen peroxide, chloride, orthophosphate, and ammonia nitrogen concentrations. The protocols for these analyses are described in detail in Appendix A.

## 2. Chemical Analysis

### a. Rationale

The approach taken in sample analysis was, to some extent, governed by requirements set forth by the Florida Department of Environmental Regulation (FDER). The approach to quantifying JP-4 and JP-4 constituents consisted of analysis of soil and groundwater samples for gross hydrocarbon contamination, using total organic carbon (TOC) and total petroleum hydrocarbon (TPH), and analysis of selected samples for discrete volatile and extractable organic compounds. Laboratory analysis was conducted according to a quality assurance plan approved by FDER (Reference 20).

To determine specific JP-4 compounds, groundwater and soil samples were analyzed utilizing a modification of EPA Methods 624 and 625: the volatiles run were extended to 60 minutes to expand the detection capability for jet-fuel-related compounds. Table 6 is a full list of all compounds that were quantified and for which standards were analyzed.

The objective of the analytical program was to generate data through which the effectiveness of the enhanced bioreclamation program could be evaluated. Compounds for inclusion in the monitoring program were selected on the basis of the results of the initial sample analyses. The reconstructed gas chromatograph/mass spectrometer (GC/MS) ion chromatograms were examined, and the compounds present in significant concentrations were tentatively identified by spectral interpretation and computerized library matching, using the EPA/NBS/NIH library. Prevalent compounds from this effort were added to the normal 624/625 compound list and determined in subsequent samples. The list was developed to include representatives of the major classes of compounds in JP-4 and their possible breakdown products.

Determination of TOC and/or TPH concentration provided a rapid and expensive means by which gross hydrocarbon contamination was determined. Initially, the intent was to use only the TPH analysis: in preference to total organic carbon, primarily because of the (hoped-for) greater level of specificity and the minimization of potential interferences: total organic carbon

TABLE 6. COMPOUNDS QUANTIFIED USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

## VOLATILES

Chloromethane  
 Bromoethane  
 Vinylchloride  
 Dichlorodifluoromethane  
 Chloroethane  
 Methylene chloride  
 Acetone  
 Acrolein  
 Acrylonitrile  
 Trichlorofluoromethane  
 1,1-Dichloroethene  
 1,1-Dichloroethane  
 trans-1,2-Dichloroethene  
 Chloroform  
 1,2-Dichloroethane<sup>a,b</sup>  
 2-Butanone  
 1,1,1-Trichloroethane  
 Carbon tetrachloride  
 Bromodichloromethane  
 1,1,2,2-Tetrachloroethane  
 1,2-Dichloropropane  
 cis-1,3-Dichloropropene  
 Trichloroethene  
 Chlorodibromomethane  
 1,1,2-Trichloroethane  
 Benzene<sup>a,c</sup>  
 trans-1,3-Dichloropropene  
 2-Chloroethylvinyl ether  
 Bromoform  
 4-Methyl-2-pentanone<sup>c</sup>  
 Tetrachloroethene  
 Toluene<sup>a,c</sup>  
 Chlorobenzene  
 Ethylbenzene<sup>a,c</sup>  
 m-Xylene<sup>a,c</sup>  
 o&p Xylenes<sup>a,c</sup>  
 2-Methylbutane<sup>c</sup>  
 t-Butyl methyl ether<sup>a,b</sup>  
 Pentane<sup>c</sup>  
 Cyclohexane<sup>c</sup>  
 3-Methylpentane<sup>c</sup>  
 Hexane<sup>c</sup>  
 Methylcyclohexane<sup>c</sup>  
 3-Methylhexane<sup>c</sup>  
 Heptane<sup>c</sup>  
 Propylbenzene<sup>a,c</sup>  
 3-Ethyltoluene<sup>a,c</sup>  
 p-Ethyltoluene<sup>c</sup>

## SEMIVOLATILES

n-Nitroso-dimethylamine  
 bis(2-Chloroethyl) ether  
 1,3-Dichlorobenzene  
 1,4-Dichlorobenzene  
 1,2-Dichlorobenzene  
 bis(2-Chloroisopropyl) ether  
 n-Nitrosodipropylamine  
 Hexachloroethane  
 Nitrobenzene  
 Isophorone  
 bis(2-Chloroethoxy) methane  
 1,2,4-Trichlorobenzene  
 Naphthalene<sup>c</sup>  
 Hexachlorobutadiene  
 Hexachlorocyclopentadiene  
 2-Chloronaphthalene  
 Dimethylphthalate  
 Acenaphthylene  
 2,6-Dinitrotoluene  
 Acenaphthene  
 2,4-Dinitrotoluene  
 Diethylphthalate  
 Fluorene  
 4-Chlorophenyl phenyl ether  
 n-Nitrosodiphenylamine  
 4-Bromophenyl phenyl ether  
 Hexachlorobenzene  
 Phenanthrene  
 Anthracene  
 di-N-butyl phthalate  
 Fluoranthene  
 Benzidine  
 Pyrene  
 Butyl benzyl phthalate  
 3,3'-Dichlorobenzidine  
 Benzo(a)anthracene  
 Chrysene  
 bis(2-Ethylhexyl)phthalate  
 di-N-Octyl phthalate  
 Benzo(b&k)fluoranthene  
 Benzo(a)pyrene  
 Indeno(1,2,3-cd)pyrene  
 Dibenzo(a,h)anthracene  
 Benzo(g,h,i)perylene  
 Phenol<sup>d</sup>  
 2-Chlorophenol  
 2-Nitrophenol  
 2,4-Dimethylphenol<sup>d</sup>

TABLE 6. COMPOUNDS QUANTIFIED USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY  
(CONCLUDED)

VOLATILES

1,3,5-Trimethylbenzene<sup>c</sup>  
1,2,4-Trimethylbenzene<sup>a,c</sup>

SEMIVOLATILES

2,4-Dichlorophenol<sup>d</sup>  
4-Chloro-3-methylphenol  
2,4,6-Trichlorophenol  
2,4-Dinitrophenol  
4-Nitrophenol  
4,6-Dinitro-2-methylphenol  
Pentachlorophenol  
2-Methylphenol<sup>d</sup>  
4-Methylphenol<sup>d</sup>  
Benzoic acid<sup>d</sup>  
2-Methylnaphthalene<sup>a,c</sup>  
1-Methylnaphthalene<sup>a,c</sup>  
2,6-Dimethylphenol<sup>d</sup>  
Octanol<sup>d</sup>  
2,4-Dimethylbenzoic acid<sup>d</sup>  
2-Methyl octane<sup>c</sup>  
2,3-Dimethyl heptane<sup>3</sup>  
Octanoic acid<sup>d</sup>  
Octane<sup>c</sup>  
Nonane<sup>c</sup>  
Decane<sup>c</sup>  
Undecane<sup>c</sup>  
Dodecane<sup>c</sup>  
Tridecane<sup>c</sup>  
Tetradecane<sup>c</sup>  
Pentadecane<sup>c</sup>  
Hexadecane<sup>c</sup>  
Heptadecane<sup>c</sup>  
Octadecane<sup>c</sup>  
Nonadecane<sup>c</sup>  
Eicosane<sup>c</sup>

<sup>a</sup>Compounds for which Florida Department of Environmental Regulation required analysis.

<sup>b</sup>Compounds not typically found in JP-4, however, frequently found as additives in gasoline motor fuel.

<sup>c</sup>Compounds found in JP-4.

<sup>d</sup>Possible JP-4 breakdown products.

measures all organic carbon in a sample, as opposed to the petroleum hydrocarbon determination, which is intended to be more or less specific for petroleum hydrocarbons. It was believed that use of the total organic carbon method for the demonstration could be problematic, because of the presence of naturally occurring organics in the form of peat and other decomposing vegetative matter. Initial sampling indicated that the TPH analysis appeared reasonable for soil analysis but, the TPH values for water samples appeared to be quite low and not well correlated with GC/MS analysis. It was therefore decided to use TPH analysis for soils and TOC for water. TOC background levels were generally less than 15 mg/L in groundwater and did not appear to interfere with hydrocarbon contamination analysis.

Total petroleum hydrocarbon concentrations were determined according to EPA Method 418.1. Samples were extracted into freon, passed through silica gel to remove nonpetroleum hydrocarbons, and quantified with an infrared spectrometer. Aqueous samples were extracted with a separatory funnel; soil samples, with a Soxhlet extractor.

### 3. Microbial Analysis

Soil and groundwater samples were tested for the densities of total heterotrophic bacteria and of hydrocarbon-degrading bacteria. Microbial enumerations were based on modifications of the heterotrophic plate count, spread plate method (Reference 21). Groundwater samples were prepared for enumeration by performing serial decimal dilutions of the sample in a sterile mineral-salts broth. Subsurface soil samples were prepared by homogenizing 6 gms of soil in 50 mls of a mixture of 1% sodium pyrophosphate, 0.1% polyvinylpyrrolidone-360 (PVP-360), followed by serial decimal dilutions. Homogenization was done in two 15-second intervals at high speed in a Waring blender, separated by a 15-second rest period. Homogenization in the pyrophosphate-PVP solution was designed to facilitate the release of bacteria attached to soil particles. This method is a modification of that reported by Balkwill and Ghiorse (Reference 22).

Aliquots (0.1 ml) of the appropriate dilutions were plated on differential agar media. The concentration of total heterotrophic bacteria is defined as the number of colony-forming units (CFU) per milliliter of groundwater per gram dry weight of soil that can form macroscopically visible colonies on 0.23% Nutrient Agar (BBL or Difco) after one week incubation at ambient temperature and oxygen. Hydrocarbon-degrading bacteria are defined as those capable of forming colonies on carbon-free mineral-salt agar when incubated under a hydrocarbon-vapor atmosphere at ambient temperature for 1 week (Reference 23).

### SECTION III

#### LABORATORY STUDIES AND SYSTEM DESIGN

##### A. LABORATORY STUDIES

###### 1. Bench-Scale Microcosms

One of the tasks typically undertaken in the laboratory phase of an enhanced bioreclamation project is to conduct a bench-scale degradation study, using contaminated soils and groundwater from the site, to determine the effects of nutrient and oxygen supplementation on the rate of contaminant biodegradation, and to estimate the extent of contaminant removal that is achievable biologically under laboratory conditions. These studies have historically been conducted in batch reactors, or microcosms, which consist of soil/groundwater slurries in sealed glass vessels. The microcosms are treated with the appropriate nutrient and hydrogen peroxide amendments, and one set of microcosms is sterilized and/or inhibited with a biological poison to account for physical/chemical mechanisms for contaminant removal from the system. Aqueous samples can then be periodically withdrawn for microbial, nutrient and/or contaminant analyses, or the entire reactor can be sacrificed for analysis. While studies such as these provide a limited model of the natural aquifer environment, the resultant information may be useful in determining the relative effectiveness of different nutrient types and their concentrations on biodegradation rates, and for demonstrating contaminant biodegradability.

For reasons of simplicity and cost, most microcosm degradation studies monitor only aqueous-phase contaminant biodegradation. For the Eglin project, it was found that more meaningful results were obtained when the soil and groundwater hydrocarbon material within the reactors was analyzed.

###### a. Initial Microcosms

The first microcosms were prepared by combining 20 gms of contaminated soil and 20 mls of site groundwater in a 40-ml VOA vial. Vials were tightly sealed and nutrients injected through a septum to determine their effect. Excess oxygen was maintained through hydrogen peroxide additions. The microcosms were separately analyzed: the aqueous fraction was extracted with pentane and analyzed by capillary GC-FID. The soil underwent Soxhlet extraction according to Standard Method 503D, followed by analysis of the extracts with a capillary GC-FID.

A GC/FID analysis of the aqueous phase appeared to show that biodegradation was enhanced by 25 ug/L concentrations of Restore<sup>R</sup> 375 nutrient solution (Table 8) and that the total extractable organics were degraded from 35 ppm to <0.2 ug/L in nine days. Unfortunately, substantial hydrocarbon disappearance was also noted in the dead controls. Analysis of the solid phase (soils) exhibited considerable noise, and because of extraction problems it actually indicated an increase in organics. This analytical procedure cannot be reliably used to measure biodegradation of low-solubility compounds adsorbed or occluded in soils.

TABLE 8. HYDROGEN PEROXIDE STABILITY TEST<sup>a</sup> RESULTS

Time (Min)	Respike Test <sup>b</sup>		Phosphate Pretreatment Test		
	Initial	Respike	None	0.05 Percent	1 Percent
0	293	307	571	555	571
30	-	-	471	513	508
60	221	-	416	489	-
90	-	-	387	-	505
120	-	-	-	455	-
180	216	-	-	413	471
210	-	-	282	-	-
240	-	320	-	387	-
270	-	-	-	-	461
300	-	-	-	361	-
360	147	289	-	356	-
1140	-	-	61	-	-
1320	24	-	-	-	360
1440	-	-	-	122	-
4230	-	8.2	-	-	-
k <sup>c</sup>	0.0019	0.00089	0.0018	0.0010	0.00029
t <sub>1/2</sub> <sup>d</sup>	370	780	370	680	2400

<sup>a</sup>Test conducted with a 33 percent soil slurry using Restore<sup>TM</sup> 105, a 35 percent peroxide solution.

<sup>b</sup>After a 24 hour exposure to hydrogen peroxide the same sample was respiked for a second test.

<sup>c</sup>k = First order decay constant (mg/L.min).

<sup>d</sup>t<sub>1/2</sub> = Half life (min).

#### b. Follow-Up Microcosms

Following several failed attempts at bench-scale studies as described above, the study was repeated using a modified purge-and-trap procedure to detect hydrocarbons in both phases. These studies did succeed in determining nutrient effects.

##### (1) Treatments

Contaminated soil was collected from the Eglin POL site that appeared to be relatively free of silt and humic material. A composite of the groundwater was collected from each of the recovery wells. Soils were homogenized by repeated passing through a narrow-mesh screen at a temperature of approximately 4°C. The homogenized soil and the composite groundwater sample were then mixed in a large polyethylene container, and any free-phase contaminant was skimmed from the surface with a suction apparatus. This procedure was repeated until no free-phase contaminant was evident on the water surface. The mixture was then left to equilibrate under refrigerated conditions for 24 hours.

Following this period, the soil and aqueous phases were again separated. The soil phase was rehomogenized, and then aliquots of each phase (5 grams soils; 50 milliliters groundwater) were measured into the incubation/sampling vessels. After filling, all openings of the vessel were sealed using Teflon-faced septa. After initial preparation, amendments were added to sets of microcosms in accordance with the various treatment conditions. A biologically inhibited control, a condition with 100 mg/L of Restore<sup>R</sup> 375 (Table 7) and one with no nutrient addition were tested.

Biologically inhibited controls were dosed initially and at 1-week intervals with sodium azide to inhibit microbial activity. These controls were used to indicate the extent of contaminant loss from abiotic mechanisms and to evaluate potential chemical oxidation of the contaminant resulting directly from the peroxide amendment. The extent to which the availability of inorganic nutrients ( $\text{NH}_4^+$  and  $\text{PO}_4^-$ ) was limiting contaminant biodegradation was determined by comparing microcosms that received no nutrient supplementation to those that are amended with Restore<sup>R</sup> 375 microbial nutrient.

Since the organic concentrations within each microcosm should have been approximately equal at the start of the study, three microcosms, selected at random, were analyzed to determine this initial concentration. Afterwards, one microcosm from each treatment condition was sacrificed for analysis, at a rate of approximately one per week.

## (2) Analytical Methodology

An analytical methodology was devised which permitted the simultaneous quantification of the hydrocarbon within the soil and water matrix of each microcosm. A purge-and-trap technique was used to extract the purgeable hydrocarbon fraction and concentrate it on an activated-carbon adsorbent. The adsorbed contaminant is then extracted from the activated carbon with carbon disulfide, and the extract was analyzed by high-resolution capillary gas chromatography using a flame ionization detector (FID).

TABLE 7. COMPOSITION OF RESTORE 375<sup>R</sup> THE INORGANIC NUTRIENT BLEND UTILIZED IN THE EGLIN AFB ENHANCED BIORECLAMATION DEMONSTRATION

<u>Component</u>	<u>Percent Composition by Weight</u>
Ammonium chloride	50.0
Disodium phosphate	20.0
Trisodium tripolyphosphate	17.5
Monosodium phosphate	12.5

## (3) Results

Analytical results of the biodegradation study are shown in Figure 4. The data show a significant hydrocarbon reduction in both of the living treatment conditions. In general, contaminant concentrations remained at low, but detectable, levels at the conclusion of the study. In the treatment receiving 100 ug/L of Restore<sup>R</sup> 375 however, the contaminant mass was reduced to below detection after 40 days. The reduction of hydrocarbon mass in the biologically inhibited controls was more gradual than that observed within the living microcosms, possibly as the result of volatilization loss. More than half of the contaminant remained in these controls at the conclusion of the study.

Periodic monitoring of pH, nutrient, and nitrate concentrations showed relatively stable conditions throughout the 40-day incubation period. Additional supplementation of nutrients was not necessary, and it was not necessary to adjust (pH remained at or about 6.5 throughout the study).

Results of the microcosm study provide evidence of the biodegradability of the extractable fraction of the jet fuel contaminant. Biological consumption appeared to account for much of the estimated 90+% reduction in hydrocarbon mass after 40 days of incubation.

There was no discernible difference in the extent or rate of biodegradation as the result of nutrient amendment. This is probably the result of sufficient nutrient in the untreated soil/water sample matrix. Analytical data showed background nitrogen and phosphorus concentrations of the groundwater used in the study to be 6.1 mg/L and 0.9 mg/L, respectively (present as ammonia and orthophosphate). The concentration of these nutrients in the soil matrix was equivalent to 15.2 mg/L ammonium nitrogen and as detectable phosphate. Adjusting for the respective weight contributions of each matrix yields average background nutrient concentrations within each microcosm of 6.9 mg/L and 0.8 mg/L of nitrogen and phosphorus, respectively. Assuming that a nutrient ratio of 100:10:1 of carbon, nitrogen, and phosphorus (by weight) is sufficient to sustain heterotrophic microbial activity, it appears that sufficient background nutrients were available to degrade the contaminant mass within each of the microcosms.

## 2. Hydrogen Peroxide Stability

The conversion of hydrogen peroxide to oxygen and water is catalyzed by bacterial enzymes (Reference 24) and by certain soils, organics, and inorganics. The rate of decomposition depends on the chemical composition of the soil, bacterial populations, and the presence of reduced organics and metals. The stability of hydrogen peroxide may be improved in the presence of phosphates (Reference 25). In an attempt to evaluate the stability of hydrogen peroxide under the conditions that would be present during a bioreclamation program at the Eglin site, soil was taken from the permeameter at the conclusion of the nutrient transport study (see Section III.A.3) and slurried in a 1:3 ratio with a 500 ug/L solution of Restore<sup>R</sup> 375 and deionized water. A 35 percent solution of stabilized hydrogen peroxide was then added to the slurry to give a final H<sub>2</sub>O<sub>2</sub> concentration of about 290 mg/L. Aliquots were periodically withdrawn and analyzed for hydrogen peroxide by the titanium sulfate method (Appendix A). As shown in Table 8, about half of the hydrogen

- Biologically Inhibited with Hydrogen Peroxide
- Biologically Inhibited without Hydrogen Peroxide
- Biologically Active without Nutrient Addition
- Biologically Active with Nutrient Addition  
(100 mg/l Restore<sup>®</sup> 375)

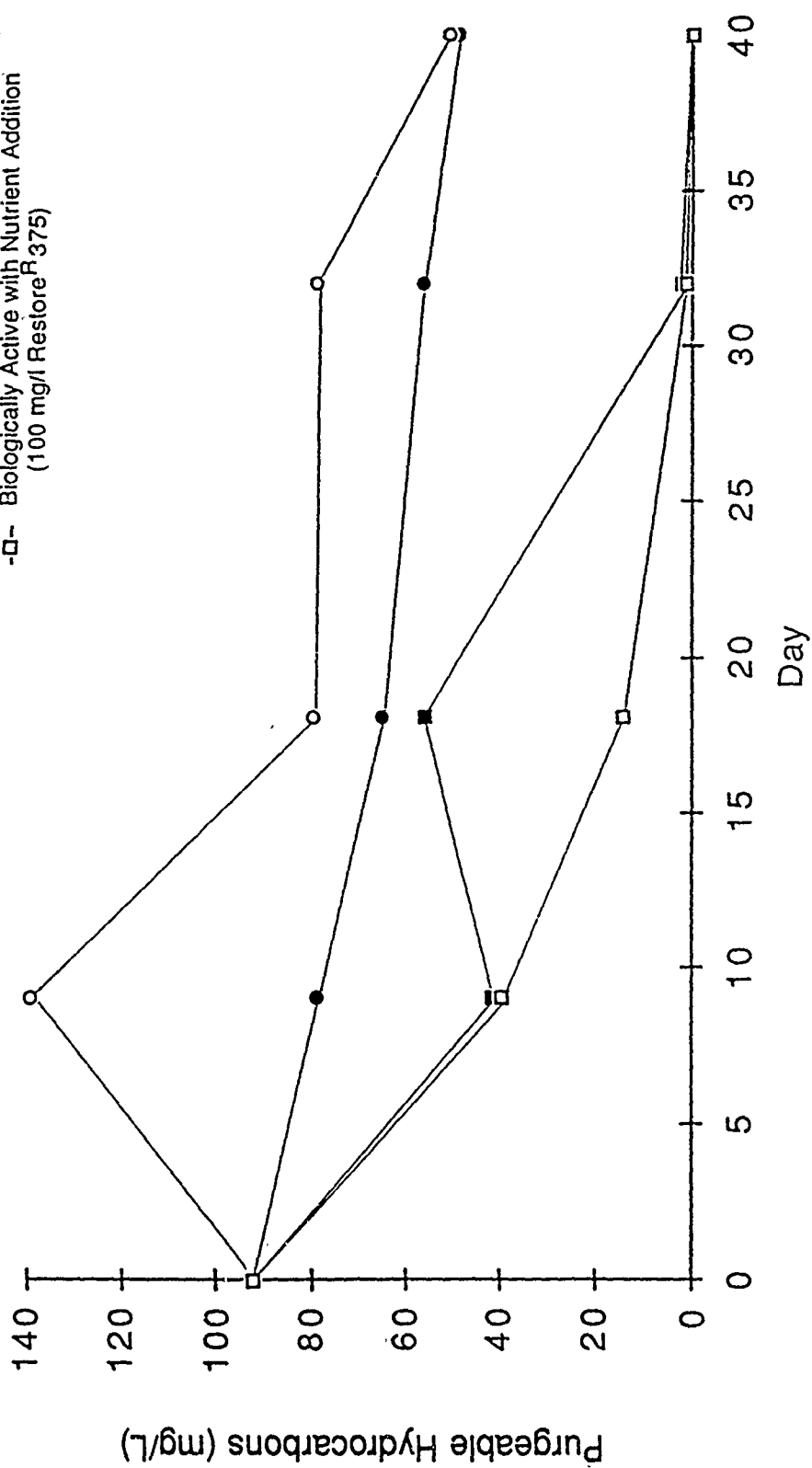


Figure 4. Results of the Bench-Scale Microcosm Biodegradation Study (concentrations reported as mg/L of n-hexane equivalents).

peroxide decomposed within 6 hours of the initial exposure. When a second dose of hydrogen peroxide was added to the slurry, less than 5 percent of the hydrogen peroxide decomposed after 6 hours. The results of this test appeared to indicate the oxidation of some constituent in the soil water system on the initial exposure to hydrogen peroxide: a lower concentration of the available un-oxidized material (possibly iron) in the slurry may have created a lower rate of  $H_2O_2$  consumption with the second addition. Operationally, this finding was interpreted to indicate that addition of hydrogen peroxide in the field should be instituted at a low concentration and slowly increased to avoid excessively rapid decomposition of the  $H_2O_2$  and potential gas blockage of the formation. As will be discussed subsequently, this was not the case. It was also assumed that this would enable the microbial populations to adapt to the presence of peroxide.

Peroxide stability tests were conducted to determine whether hydrogen peroxide decomposition would occur at a slower rate in soils that had been exposed to Restore<sup>R</sup> 375, which contains stabilizing phosphates. To test this, three slurries of Eglin POL site soil were prepared, two in concentrations of Restore<sup>R</sup> 375 (0.05 percent and 1.0 percent, in deionized water), plus one untreated slurry (deionized water only). The slurries consisted of 100 grams of soil in 200 ml of the appropriate solution. The slurries were stirred overnight, after which they were allowed to settle, the supernatant decanted and the residual liquid drained. Thirty grams of each soil was then placed into a flask and 90 ml of composited site groundwater was added to each flask.  $H_2O_2$  was then added to these slurries to give final concentrations of 500 mg/L of  $H_2O_2$ . Samples for analysis of  $H_2O_2$  concentration were taken initially and at various times thereafter. Dissolved oxygen in the flasks was measured at each sampling with a Yellow Springs Instruments dissolved oxygen (DO) meter.

The results indicated that peroxide decomposed much more rapidly in the presence of the untreated soils. The initial rate of decomposition was retarded in the soils treated with 0.05 percent Restore<sup>R</sup> 375, but the decomposition rate after six hours paralleled that of the untreated soil.

When the soil was treated with 1 percent Restore<sup>R</sup> 375 (the concentration frequently used in the field study injection water) the stability of the peroxide was further improved (Table 8). Measurement of DO in the peroxide-spiked slurries likewise showed a slower increase in DO level in the 1 percent Restore<sup>R</sup> 375 treatment. This part of the experiment was hampered by the inability of the dissolved oxygen meter to measure oxygen levels above 20 mg/L. Thus, it was not possible to calculate a mass balance of oxygen and peroxide in the system to take into account the possibility of direct consumption of  $H_2O_2$ . Nevertheless, the results appeared to indicate that catalytic decomposition was a significant fate of hydrogen peroxide in soil and groundwater, and that the rate of decomposition could be influenced, but not significantly reduced, by the presence of Restore<sup>R</sup> 375 nutrients.

It should be noted here, as is discussed in Section IV B, that these laboratory tests did not adequately predict the field performance of hydrogen peroxide. Subsequent work by Lawes (Reference 26) indicates that utilizing a soil-to-water ratio that is closer to the natural conditions (i.e., 3 parts soil:1 part water) will result in markedly different results. The validity of using diluted soil batch studies for predicting field hydrogen peroxide stability performance is questionable.

### 3. Nutrient Transport

A nutrient transport test was conducted using a Soil Test, Inc., Model K-605 Permeameter to determine the sorptive characteristics of the soil for the microbial nutrients and to provide a general indication of the permeability of the subsurface material. A composite of the soil samples collected from the site was used to fill the permeameter column, and deionized water was passed through the soil under constant head to establish a baseline flow rate. Restore<sup>R</sup> 375 microbial nutrient was dissolved in deionized water at a concentration of 500 mg/L and passed through the soil at a flow rate of approximately 3.0 to 5.0 ml/min until the concentration of nutrients in the recovered water approached that of the feed.

Figure 5 shows the results of the test of the nutrient transport through the permeameter column. Chloride was detected in the effluent almost immediately, and reached equilibrium at the feed concentration after about eight pore volumes of throughput. Ammonium and phosphate, however, were more strongly retained by the soil. Ammonium was not detected until three pore volumes of nutrient solution had passed through the column, gradually increasing in concentration and reaching equilibrium at about 14 pore volumes. Phosphate, which did not show up in the effluent until four pore volumes of solution had been collected, approached equilibrium more rapidly than ammonium, leveling off at approximately 11 pore volumes. This pattern of retention is typical of a soil that is composed primarily of sand and silt.

These results were interpreted to indicate that transport of these nutrients could be achieved at the Eglin POL site. It was believed that the moderate retention of both phosphate and ammonium might be beneficial in maintaining a fairly constant level of nutrients in the treatment area during the batch addition process. The results were also interpreted to indicate that additional phosphate could be injected in an effort to control hydrogen peroxide decomposition. The nonretention of chloride allowed its use as a tracer of groundwater flow.

Certain materials in soil and groundwater, such as iron, calcium, and magnesium, have the potential for forming precipitates when combined with the ammonium and phosphate salts of the microbial nutrient solution. To test whether this was likely to occur at the Eglin POL Demonstration site, the concentrations of total iron, calcium, and magnesium were measured in a composite water sample. Calcium was found to be present at 54 mg/L; iron at approximately 7.0 mg/L; and magnesium levels were at the detection limit of <4.0 mg/L. To test for precipitation, 100 ml of composite water was spiked with Restore<sup>R</sup> 375 microbial nutrient to give the final solution a concentration of approximately 4,500 mg/L. After 24 hours, only a slightly cloudy condition was observed in the solution. The results of this test were interpreted to indicate that nutrient additions could be made without significant precipitation, provided that nutrients were injected batchwise and the concentration of nutrient in the injection water did not fall below 0.4 percent.

It should be noted here that although these bench-scale experiments did assist in estimating chloride and ammonium transport rates, they did not accurately predict problems of injection system plugging encountered in the field. As is discussed in Section II.A, both the injection wells and the

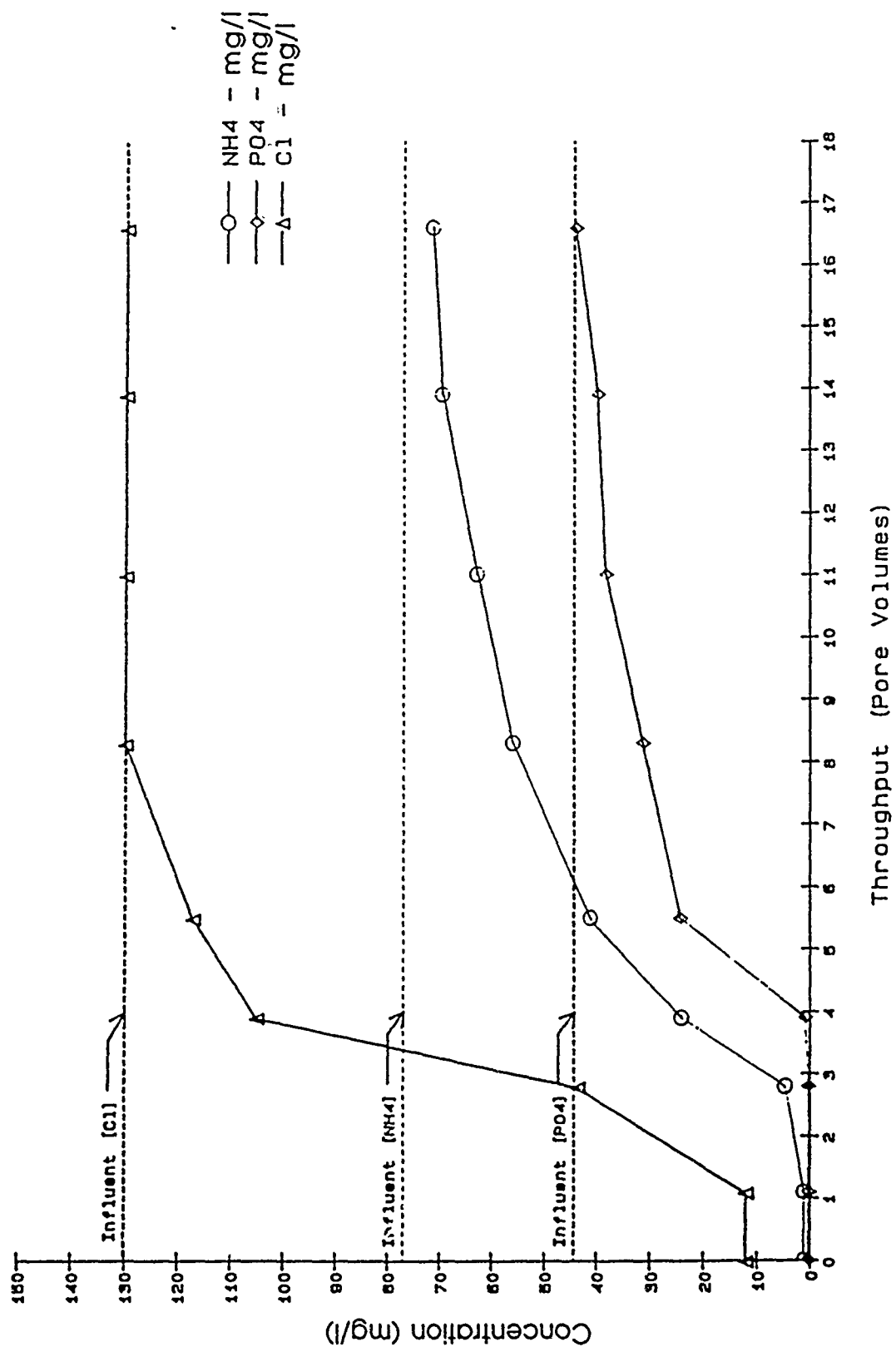


Figure 5. Results of Bench-Scale Nutrient Transport Testing in Soils Collected from the Eglin POL Demonstration Site.

infiltration galleries plugged, reducing flow rates. Despite batch additions of nutrients, the bench-scale experiments described here did not predict that plugging.

## B. SYSTEM DESIGN

### 1. Free-Product Recovery

As discussed in Section I.B., the Air Force implemented a free-product recovery program at this site in 1984. That design consisted of a series of shallow trenches with a passive-type (no groundwater pumpage) skimmer recovery system. This performed very well, and resulted in removal of essentially all recoverable free product. However, due to the intermittent recurrence of thin layers of free product in several wells, it was determined that additional free product recovery would be attempted.

Because the occurrence of free product was intermittent, the fully portable R.E. Wright AUTOSKIMMER<sup>TM</sup> was chosen for initial free-product recovery efforts. Figure 6 illustrates the AUTOSKIMMER<sup>TM</sup> and its operating principles. The key feature of the AUTOSKIMMER<sup>TM</sup> which led to its selection was that it is easily moved from well to well.

After the initial period of AUTOSKIMMER<sup>TM</sup> operation, free-product recovery was continued by means of hand bailing. Recovered JP-4 was placed in 55-gallon drums for storage. The fuel was removed by the Air Force to be used for fire training. The volume of free product recovered from each well was recorded.

### 2. Extraction/Injection Systems

The design of the extraction and injection systems are crucial to the success of any groundwater remediation effort. The design objective of groundwater extraction and reinjection systems must be to move a sufficient volume of water through the contaminated zone to transport the oxygen and nutrients necessary to allow biodegradation to occur. This, of course requires that the oxygen- and nutrient-enriched injection water contact the areas of contaminated soils.

Three methods are typically used for oxygen and nutrient injection: injection wells, infiltration galleries, and surface application--each with its own advantages and disadvantages. The injection well delivers the nutrients to the groundwater most directly, but nutrients are not delivered to the unsaturated zone. A well has a small reinjection surface area and is therefore prone to clogging, and injection wells may be relatively expensive.

Infiltration galleries and surface application deliver the nutrients in a more uniform pattern and permit more effective delivery to the unsaturated zone. The key drawback to infiltration galleries and surface application techniques is the potential difficulty in delivering nutrients to the saturated zone. An impermeable or less-permeable stratum above the saturated groundwater may prevent or limit percolation. In the case of the infiltration gallery, this can be overcome by placing the system beneath the less-permeable strata.

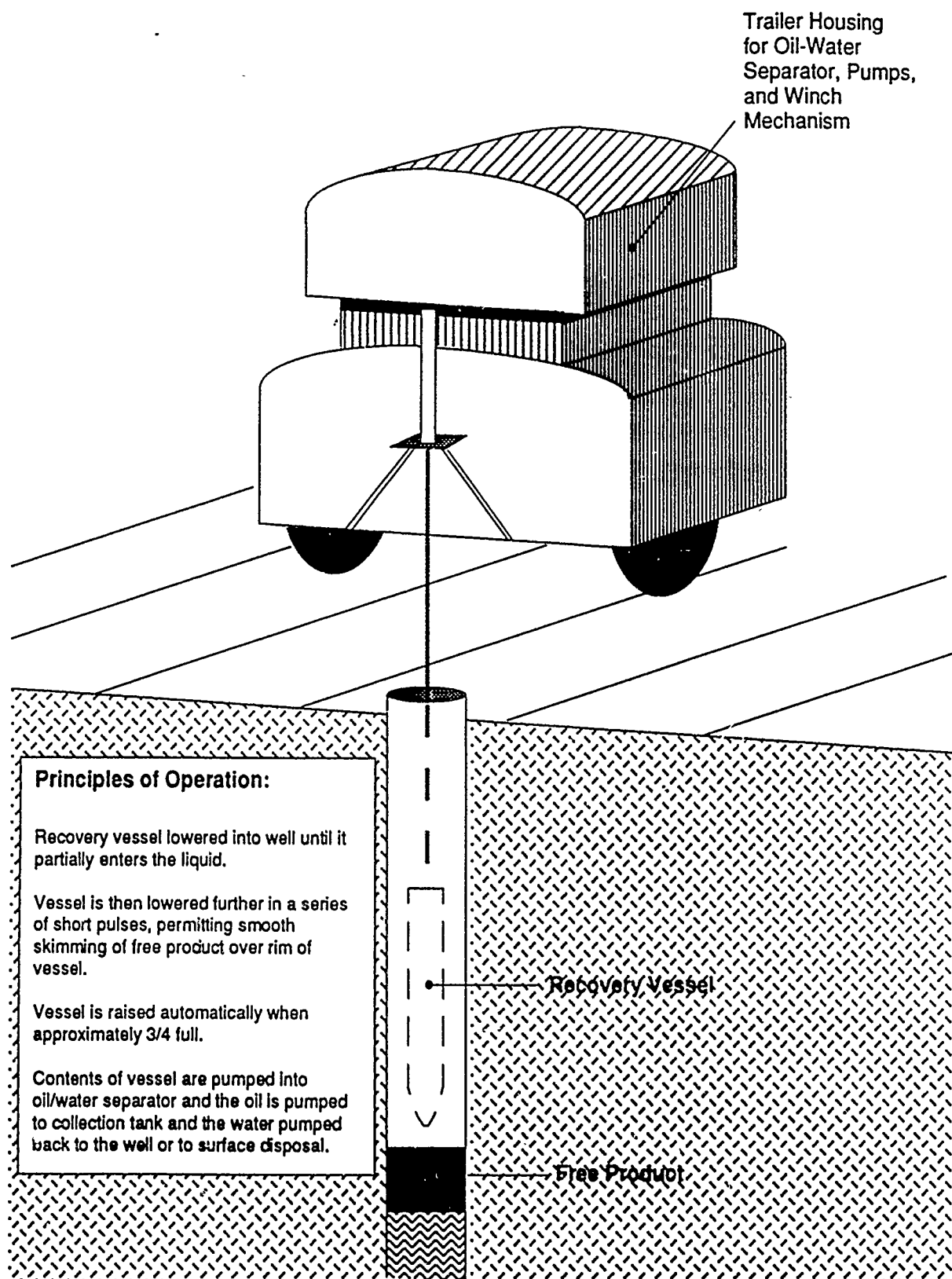


Figure 6. R.E. Wright AUTOSKIMMER™ Used for Free Product Recovery at the Eglin POL Demonstration Site.

In general, the injection well is the most expensive, the infiltration gallery is intermediate in cost, and surface application is the least expensive. In difficult situations such as paved or developed sites, or sites with relatively deep less-permeable strata, surface application may be impossible and the infiltration gallery can be substantially more expensive than an injection well.

Because the groundwater is quite shallow at the Eglin site, and the available lithological data indicated that there was no significant stratification in the unsaturated zone or the shallow saturated zone, it would appear that surface application is the technique of choice. The site, however, is amenable to all three technologies, and in the light of the research nature of this project, all three were used.

#### a. Design Basis

The injection and withdrawal systems were designed on the basis of hydraulic data from preliminary investigations by Weston (Reference 21) and Geraghty and Miller (Reference 19). Following construction of the recovery wells and injection systems, pump tests were conducted which verified the effectiveness of the design. It should be noted that the design of recovery wells and injection systems requires sufficient knowledge of the formation's permeability and potential water yield, to assure adequate design and in most cases some pump testing and an analysis of aquifer characteristics is necessary prior to design.

The Sand-and-Gravel Aquifer in the vicinity of the Eglin POL demonstration site varies from a porous, permeable sand to a less-sandy clay and clayey sand. The sand is white, fine-to-medium-grained, and poorly graded to depths of 20 feet; it becomes finer, more silty, and darker with depth. Sieve analysis of samples collected from depths of 48 and 50 feet by Geraghty and Miller (Reference 19) produced a classification of fine sand. Samples collected from borings EA5, D, EA1, and B, at depths of 5-7 feet below ground surface were classified as poorly graded sand (SP); the results of sieve analysis are attached as Appendix B. The Sand-and-Gravel Aquifer lies just beneath the land surface and is unconfined from the top; it is confined below by the relatively impermeable clay or marl of the Pensacola Clay. The water table is within 1-5 feet of the ground surface. Figure 7 is a hydrogeological cross section of the site.

After the initial installation, recovery and injection wells were tested at maximum pump yield. The results of this pump test are summarized in Table 9. In general, the treatment area can be divided into two zones on the basis of observed and calculated data, a northern zone of higher elevation (wells IN1, IN2, R1, and R2) with transmissivity of approximately 20,000 gpd/ft ( $350 \text{ m}^2/\text{d}$ ) and permeability of 270 ft/day ( $9.5 \times 10^{-2} \text{ cm/sec}$ ) and a southeastern zone of lower elevation with 10,000 gpd/ft ( $125 \text{ m}^2/\text{d}$ ) and permeability of 230 ft/day ( $4.7 \times 10^{-2} \text{ cm/sec}$ ).

The non-pumping groundwater velocity ( $v$ ) can be estimated from Darcy's Law:

$$v = Ki/n$$

figure

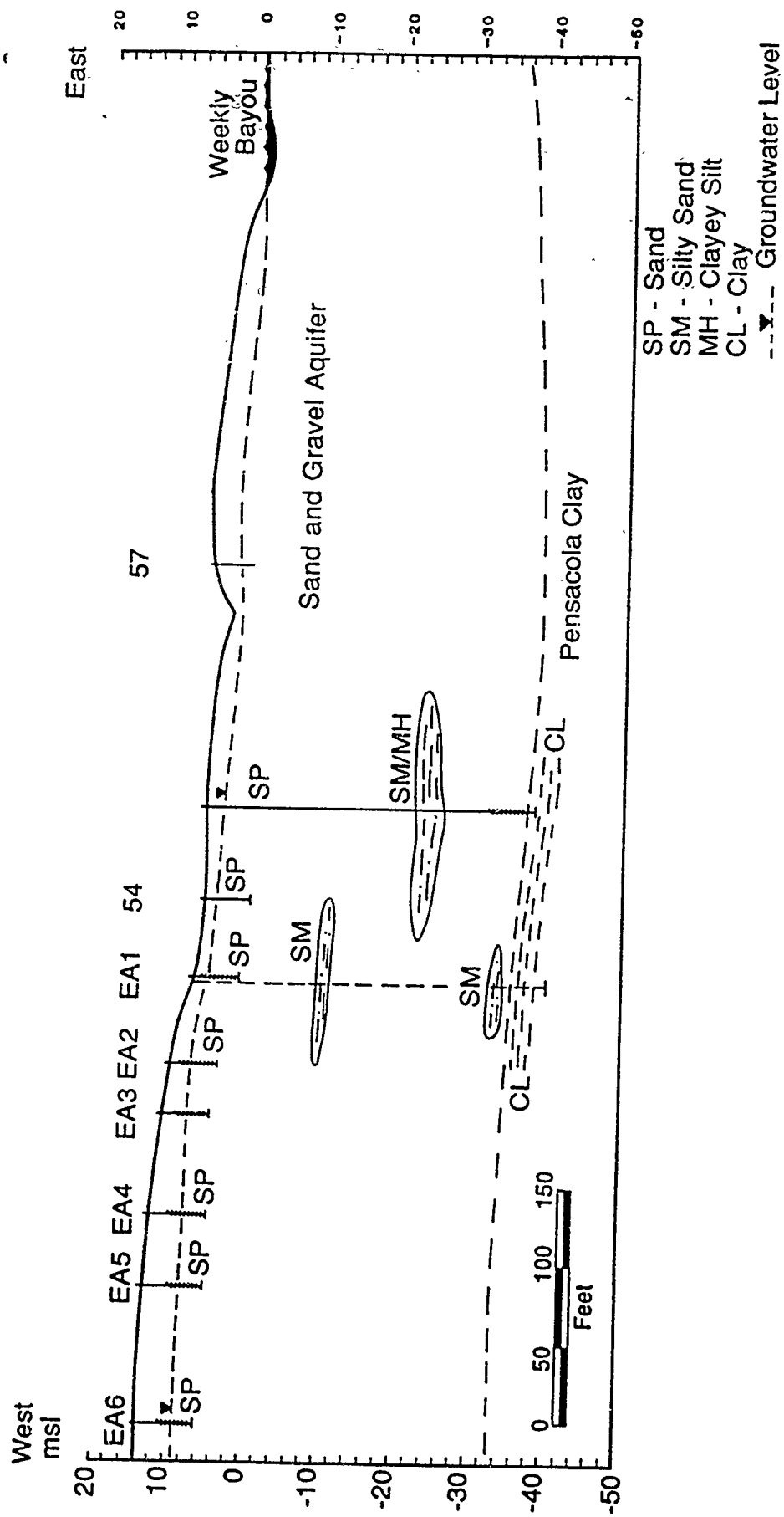


Figure 7. Hydrogeological Cross-Section of the Sand-and-Gravel Aquifer at the Eglin POL Demonstration Site.

TABLE 9. CALCULATED HYDRAULIC PARAMETERS PRIOR TO DEMONSTRATION FOR WELLS  
AT THE EGLIN POL DEMONSTRATION SITE

Well/ Observation Point	Pumping Phase T gpd/ft	Recovery Phase T gpd/ft	Pumping Phase T gpd/ft	Recovery Phase T gpd/ft	Specific Capacity gpm/ft	Hydraulic Conductivity gpd/sq.ft.	Average for Observation Point T gpd/ft	Average T m <sup>2</sup> /d	Specific Yield
IN1	12,000	17,600			6.0	2,020			
P6			18,100	22,300			20,200	250	0.065
IN2	12,400	18,600			8.3	1,540			
P2/P1			16,800 (P2)	14,000 (P1)			15,400	190	0.050
R1	15,000	30,000			8.5	1,855			
P3			20,600	16,500			18,550	230	0.040
R2	5,800	12,200			2.5	2,125			
EA1			22,000	20,600			21,250	264	0.008
R3	5,600	6,200			2.6	990			
H2			10,900	8,900			9,900	123	0.029
R4	4,800	6,400			2.4	1,090			
G1			12,900	8,900			10,900	135	0.032

where

- n = porosity (0.3)
- K = hydraulic conductivity (0.05 to 0.1 cm/sec)
- i = hydraulic gradient (0.001, based on typical non-pumping ground-water level measurements).
- v =  $1.7 \times 10^{-4}$  to  $3.3 \times 10^{-4}$  cm/sec  
= 0.5-1.0 ft/day.

The water level on the site in the Sand-and-Gravel Aquifer is 4-8 feet above sea level. Because the water is only 1-5 feet below ground surface, and the topography and permeable soils favor rapid infiltration, water levels in the Sand-and-Gravel Aquifer rise in response to any discrete rainfall event. During or soon after a heavy rain, groundwater may even be found at the surface in topographical lows. Rainfall quickly infiltrates the unsaturated surficial sands and moves down to the water table, where movement becomes predominantly lateral. The direction of groundwater flow is generally toward Weekly Bayou. Figure 8 shows the groundwater gradient.

Details of the withdrawal and injection system design are shown in Figures 9 and 10. A schematic of the design is shown in Figure 11; Figure 12 indicates the locations of the installations on site. The system consisted of four 6-inch extraction wells, two 6-inch injection wells, a series infiltration galleries, and a spray irrigation system. The contaminated area was divided into four treatment zones: an untreated control area and areas treated by each of the three application systems. This was to permit comparison of the three available technologies for groundwater injection. In addition, a small "untreated spray irrigation area" was established near EA-8 and received spray irrigation water without nutrients or peroxide.

#### b. Injection Wells

The injection wells were constructed as shown in Figure 9. The wells were screened from approximately 3 feet below ground surface to a depth of 11 feet below the groundwater surface to permit uniform nutrient distribution. The design diameter of six inches was oversized for the hydraulic needs of this site, to allow a safety factor for plugging. Although the design capacity was 5 gpm per well, initial testing indicated that the wells were capable of accepting at least 10 gpm each. The stainless steel construction permitted vigorous development, redevelopment, and screen cleaning.

A borehole of 12-inch inside diameter was drilled, using the cable tool method, to a depth of approximately 15 feet. The cable tool method did not require drilling fluid, as a protective temporary casing was used to prevent caving of the borehole.

The lower part (blank casing) was equipped with centralizers to ensure that the casing was centered in the borehole. The annular space around the casing was filled with gravel pack from the bottom of the screened interval to approximately one foot above the screen, to improve the hydraulic efficiency of the well. The well was sealed with approximately one foot of bentonite and grouted to the surface with cement.

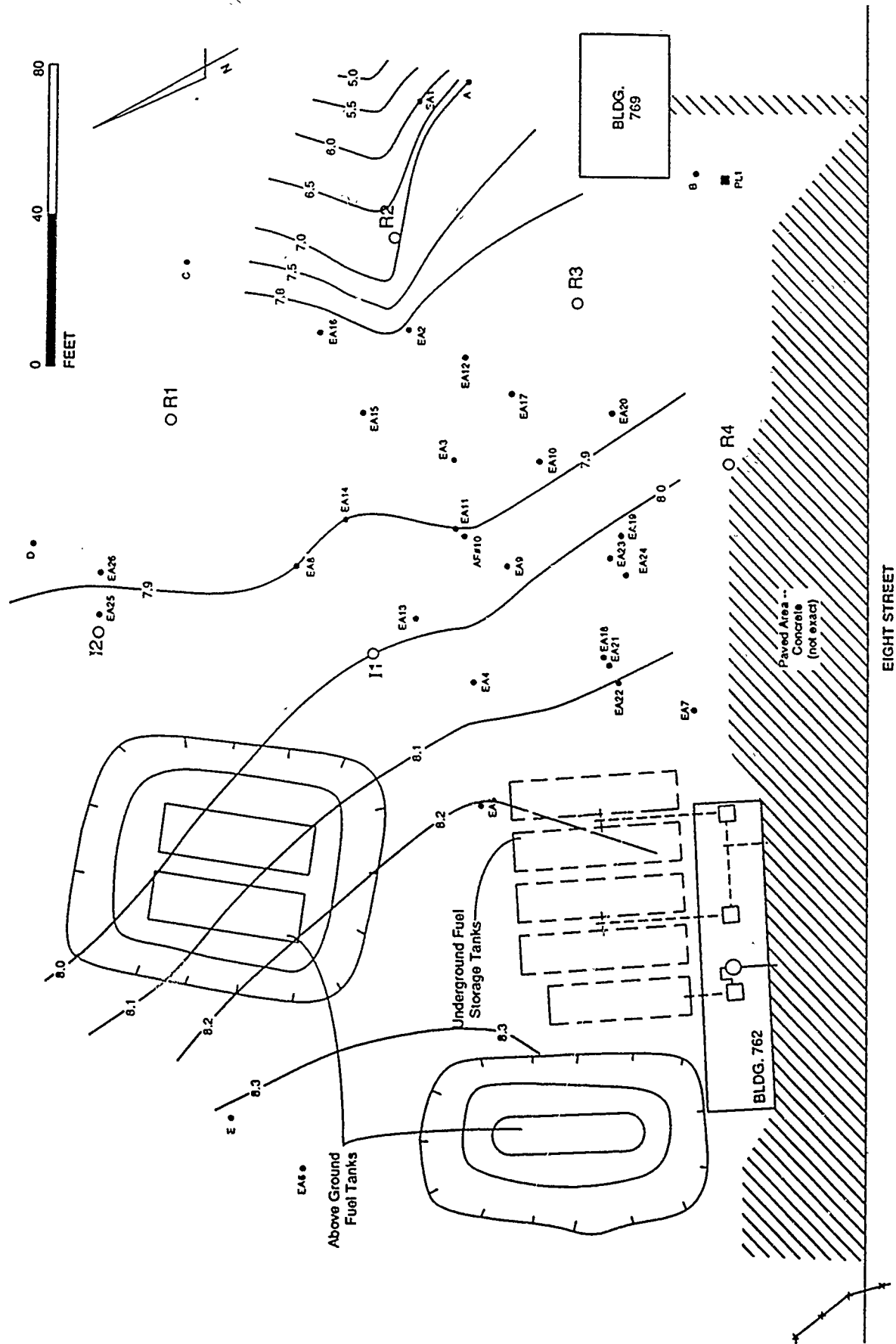


Figure 8. Groundwater Elevations at the Eglin POL Demonstration Site Under Nonpumping Conditions, 22 November 1986.

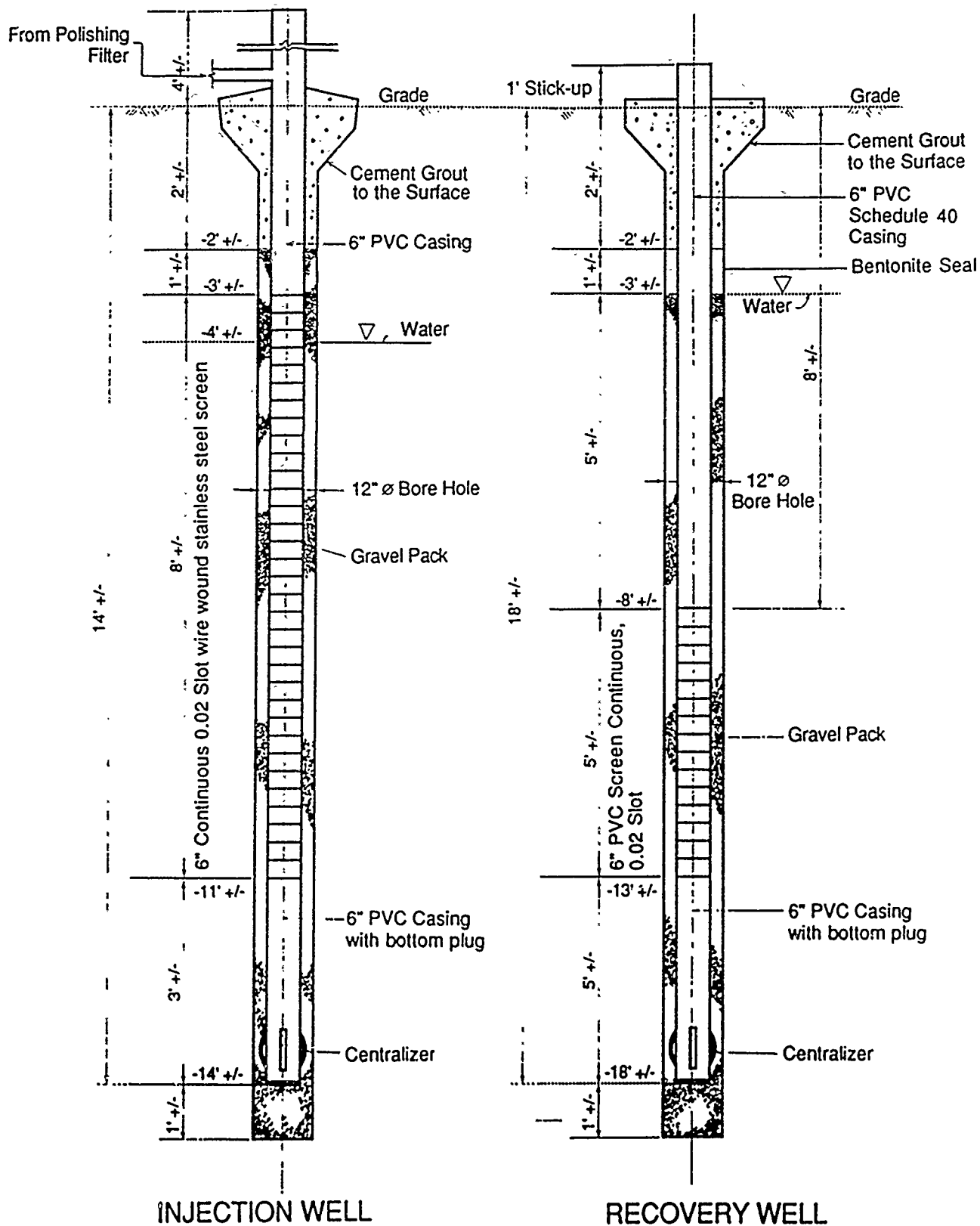


Figure 9. Injection and Recovery Well Design for Eglin POL Demonstration Site.

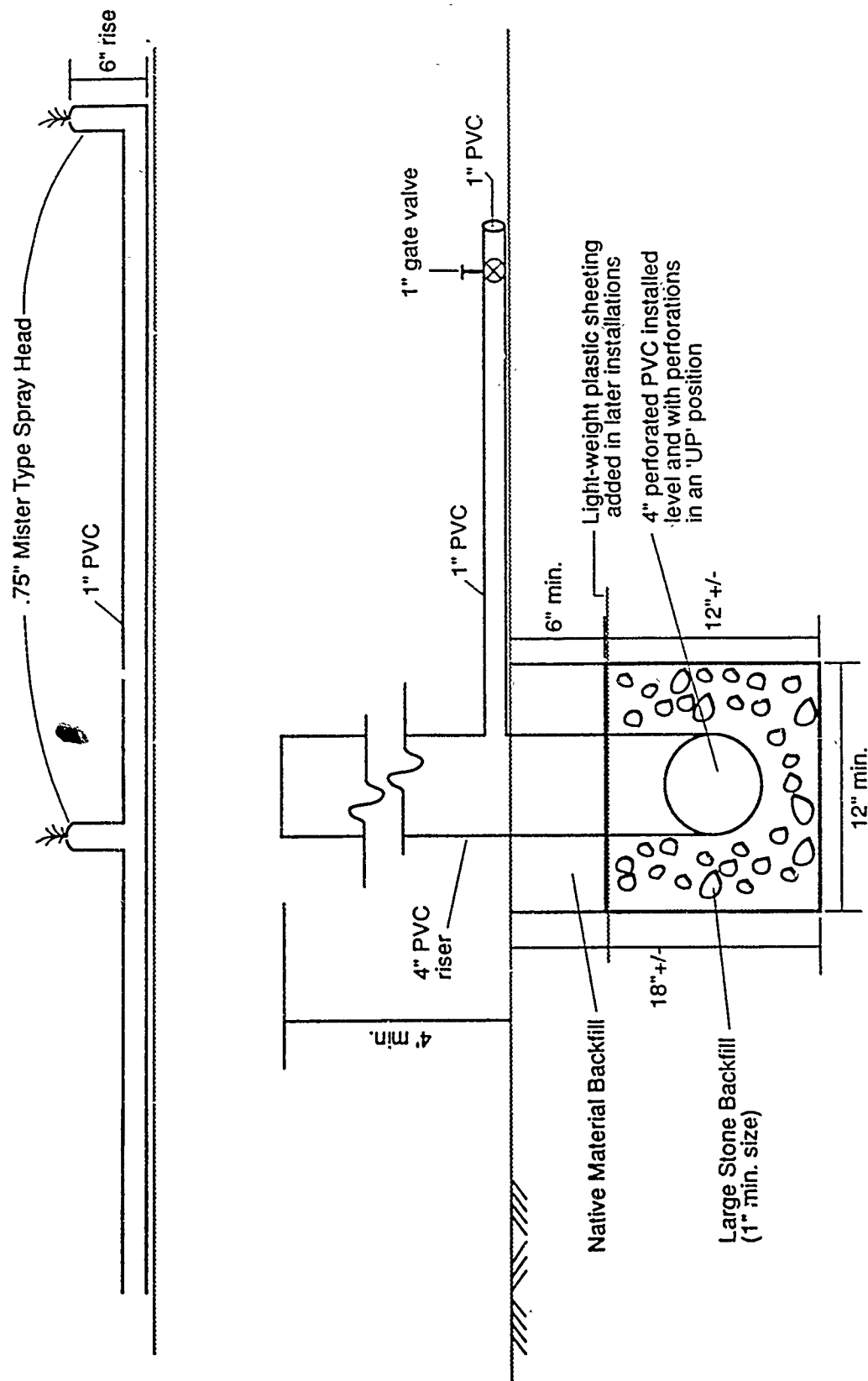


Figure 10. Spray Irrigation and Injection Gallery Design Details for Eglin POL Demonstration Site.

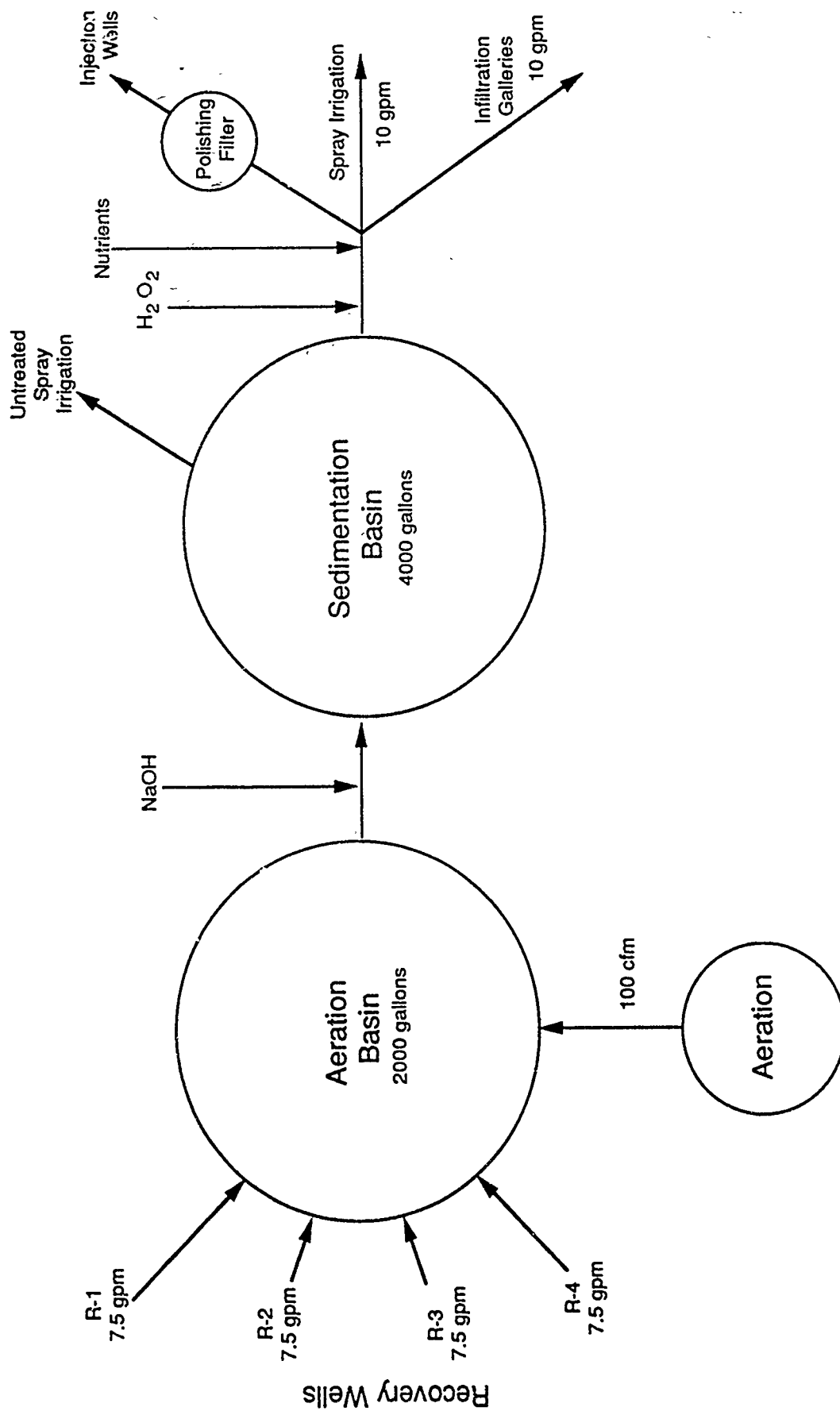


Figure 11. Design Schematic of Groundwater Treatment System for Eglin POL Demonstration Site.

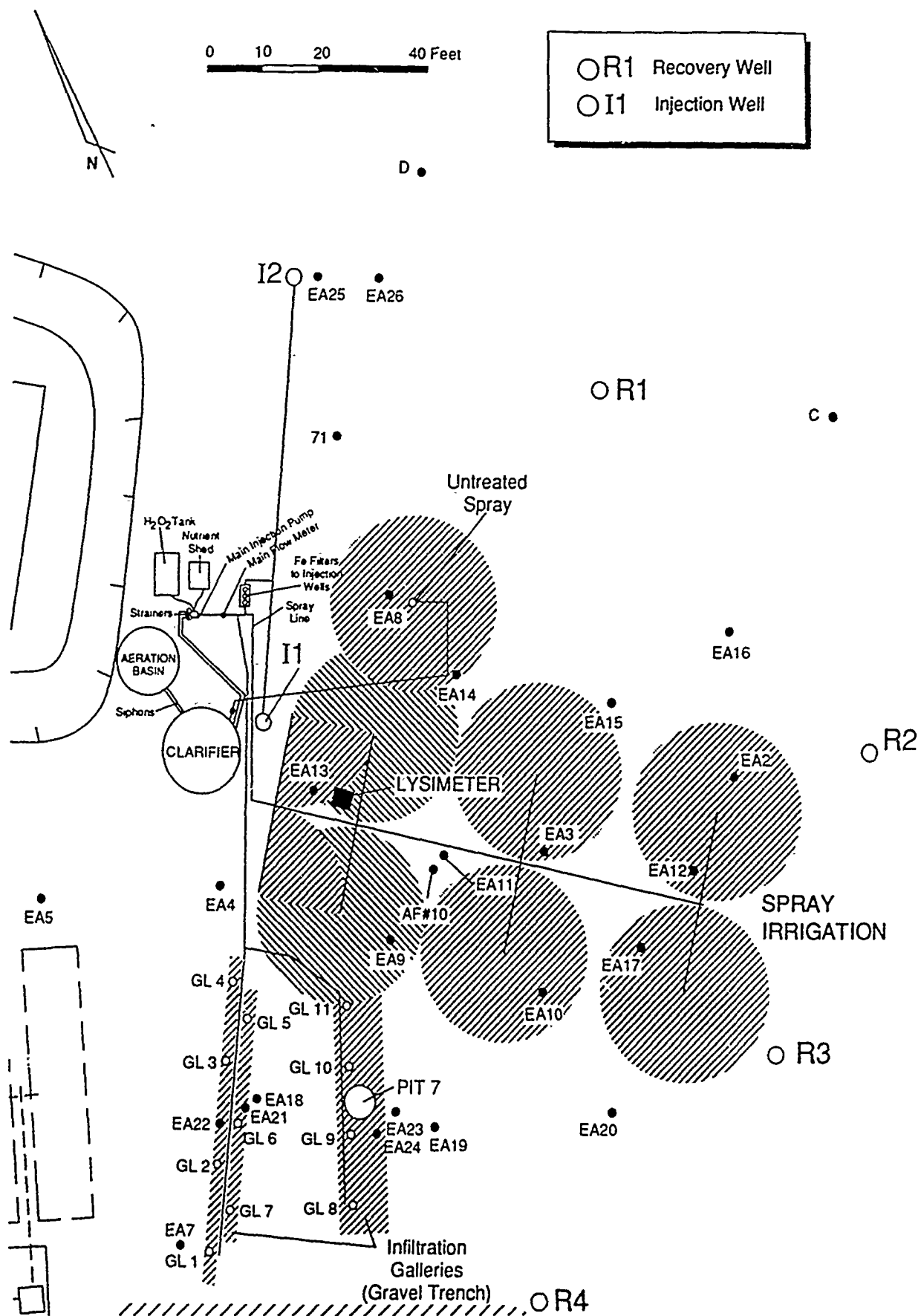


Figure 12. Locations of Treatment Facilities at Eglin POL Demonstration Site.

The wells were developed by air sparging and pumping until the water became clear and free of sand.

c. Infiltration Gallery

As shown in Figures 10 and 12, a shallow system of drains was used for infiltration. The initial design was for four galleries (GL 1, 2, 3, and 4), and initially each gallery was capable of injecting at least 2.5 gpm, for an average rate of 0.25 gal/ft/min. Subsequently, as yield was reduced additional galleries (GL 5 through 11) were constructed. Galleries GL 8, 9, 10, and 11 were located in an old gravel trench originally used to recover free product. That trench was 10 feet wide by 40 feet long and approximately 6 feet deep, containing about 5 feet of gravel overlaid by a plastic sheet.

d. Spray Irrigation

The spray irrigation system was the simplest form of reinjection. The surface application system consisted of a sprinkler system capable of covering an area of about 4,000 square feet, for an average application rate of 3.6 gal/ft<sup>2</sup>/day.

e. Extraction Wells

Four extraction (recovery) wells were used. Details of their construction are shown in Figure 9; Figure 12 shows their locations. The wells were constructed to have a screened interval of approximately 5 feet below the groundwater surface. This was to serve two purposes: to discourage free-product accumulation and to ensure nutrient movement downward through the contaminated zone. The wells were screened from approximately 8 feet below the groundwater surface to 13 feet below it. The boring was advanced 6 feet beneath the screened interval, and 5 feet of solid casing set beneath it. The purpose of this was to protect the pumps and to prevent siltation problems. A 1/3-horsepower submersible pump was installed in each well.

The extraction wells were drilled by the same cable tool method as the injection wells. Except as noted in Figure 9, construction was the same as that described for the injection wells. After installation, each well was developed by the same method as that used for the injection wells. The wells were designed to yield 7.5 gpm at a 5-foot drawdown. Initial testing indicated that a yield in excess of 15 gpm with less than 5 feet of drawdown was possible.

f. Experimental Control Areas

A contaminated area, upgradient of the nutrient and hydrogen peroxide application areas was monitored throughout the test using soil cores and groundwater sampling at EA5. The purpose of this contaminated control was to account for contaminant losses due to "natural" volatilization, leaching and biodegradation. A second control area near EA-8 received spray application without nutrients or peroxide to account for any hydrocarbon removal from the soil due to hydraulic washing alone.

### 3. Above-Ground Treatment

Following extraction and before hydrogen peroxide and nutrients were added and the water reinjected, the groundwater was treated to remove volatiles, to oxidize and remove iron, and to adjust pH. Two tanks were installed in series to receive water from the recovery wells. The configuration of these tanks is illustrated in Figure 13. The first tank, the aeration basin, was circular and approximately 3 feet deep by 12 feet in diameter, with a working volume of approximately 2,000 gallons. Air was supplied by a 3-horsepower blower through 12-inch Roeflex<sup>R</sup> diaphragm air diffusers. Air flow averaged about 100 cfm and water flow about 30 gpm. This resulted in an average detention time of approximately 80 minutes and an average air:water ratio of 25:1. Flow from the first tank into the second, the settling basin, was by gravity through three 4-inch-diameter siphons. The settling basin was approximately 3.5 feet deep by 15 feet in diameter, an average working volume of 4,000 gallons. At the average flow rate of 30 gpm, the average overflow rate for the settling basin was approximately 240 gallon/day/ft<sup>2</sup>.

Under normal operating conditions, flow into the aeration basin was constant and flow out of the settling tank was regulated by a float switch. Under pumping conditions, flow out of the settling tank was slightly greater than 30 gpm, so the water level would slowly drop until the switch turned the injection pumps off. The tank would then fill, turning the pump on.

### 4. Nutrient and Hydrogen Peroxide Injection

The design objective was to deliver sufficient oxygen and nutrients to the contamination to permit complete aerobic biodegradation of the constituents to carbon dioxide and water. Additional phosphate, in excess of nutrient requirements, was also added, in the hope that this would increase hydrogen peroxide stability.

#### a. Nutrient Addition

Nutrients were added in the form of Restore<sup>R</sup> 375, a patented commercial nutrient mixture consisting of 50 percent ammonium chloride and a blend of 20 percent disodium phosphate, 17.5 percent sodium tripolyphosphate, and 12.5 percent monosodium phosphate. Nutrient addition was designed to exceed microbial requirements. Laboratory microcosm tests, although not definitive, indicated that nutrient levels of 25 mg/L or lower would support microbial degradation. The decision to use excess nutrient addition was based on three factors: (1) the phosphate present in the nutrient solution could act to stabilize the peroxide (Reference 25); (2) laboratory column tests showed that orthophosphate precipitation in site soils was inhibited in the presence of sodium tripolyphosphate at Restore<sup>R</sup> 375 injection concentrations of at least 1,000 mg/L; and (3) an excess would ensure that oxygen alone was limiting biodegradation. One concern regarding excess nutrient addition is the potential for the precipitates formation of such as calcium phosphates, resulting in lessened well or infiltration gallery yield or reduced aquifer permeability. Nutrients were added on a batch basis. Details of the nutrient mixing and injection system are in Appendix C.

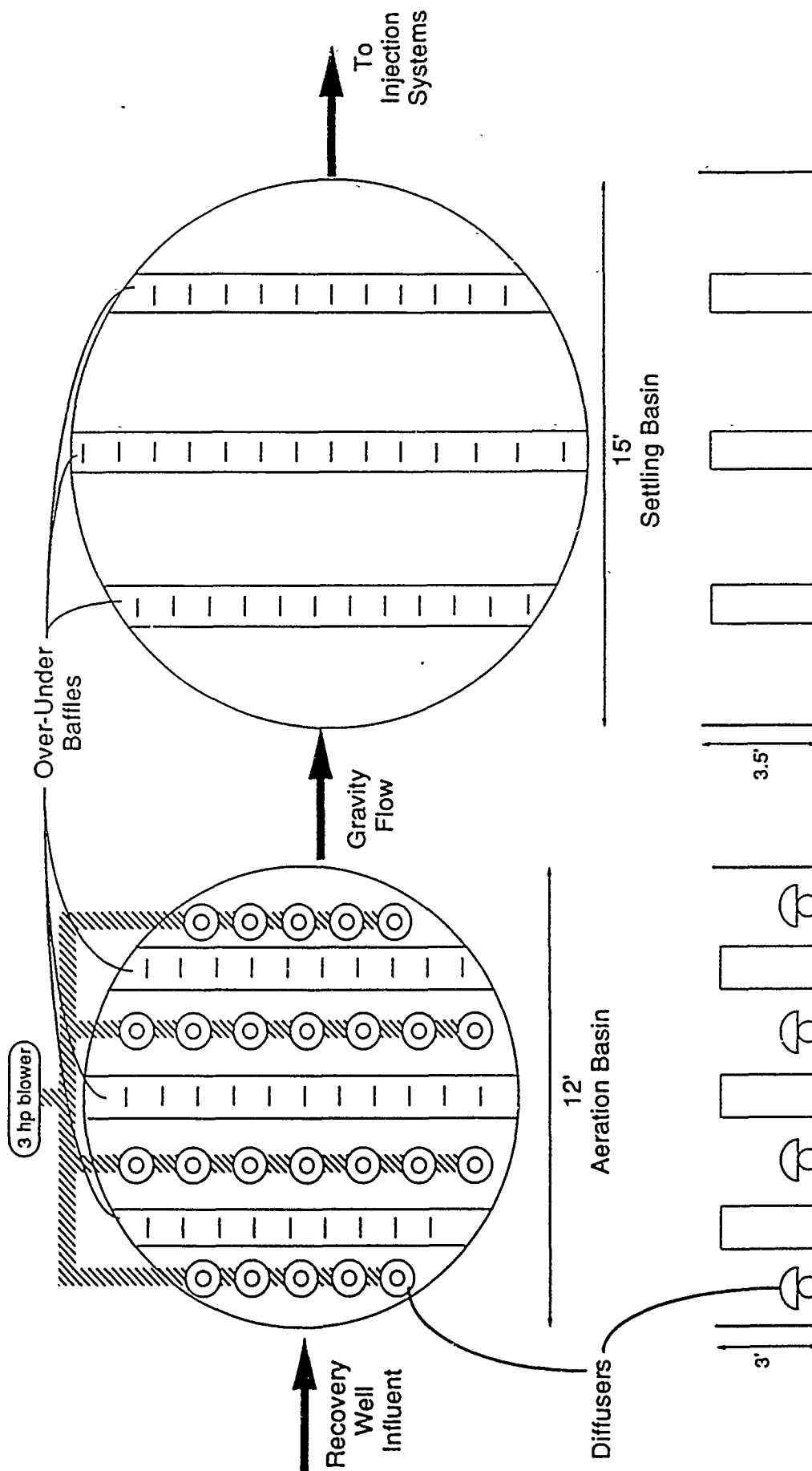


Figure 13. Configurations of Aeration and Settling Basin. Used for Groundwater Treatment at Eglin POL Demonstration Site.

b. Hydrogen Peroxide

Hydrogen peroxide was introduced in the form of Restore<sup>R</sup> 105, a patented commercial solution of 35 percent stabilized hydrogen peroxide. The term stabilized here refers to the condition of  $H_2O_2$  in the high purity aluminum tank. That is, the Restore<sup>R</sup> 105 is stable in proper storage in its pure form. The term stabilized should not be interpreted to mean that the hydrogen peroxide will necessarily be stable in groundwater.

The initial site characterization indicated that approximately 16,500 pounds of JP-4 hydrocarbons remained at the site at initiation of this project, assuming that 75 percent was within the treatment zone (excludes the control area) and that 3 pounds of oxygen would be required per pound of hydrocarbon. From this it was estimated that approximately 40,000 pounds of oxygen would have to be injected. At a flow rate of 30 gpm over a 16-month period, an average oxygen concentration of approximately 230 mg/L would have to be maintained to deliver the required oxygen. Assuming adequate stability, a hydrogen peroxide concentration of 500 mg/L could deliver approximately 250 mg/L of oxygen. On this basis, a design concentration of 500 mg/L was chosen. Hydrogen peroxide was injected on a continuous basis. Details of the hydrogen peroxide storage and injection system may be found in Appendix C.

On the basis of their past experience and the results of the laboratory testing, IT/ARS staff predicted that 500 mg/L of hydrogen peroxide could be delivered to the formation and that approximately 250 mg/L of available oxygen would be utilized for biodegradation. It should be noted here that this was not the case in the field. As discussed in subsequent sections, these assumptions did not prove to be an adequate basis for design.

## SECTION IV

### RESULTS AND DISCUSSION

#### A. FIELD OPERATIONS

##### 1. Free-Product Recovery

Figure 14 illustrates the history of free-product recovery through the life of the project. Virtually all significant recovery was in recovery well 4: the total recovery from that well accounted for 140 of the 150 total gallons recovered. During the time the AUTOSKIMMER<sup>TM</sup> was in use, there was no significant difference in performance over hand bailing. It appears that although the AUTOSKIMMER<sup>TM</sup> was capable of recovering product, hand bailing was equally effective. It should be noted that a full-time field person was available on this site to hand bail. If manual bailing were less convenient or if a site consistently had greater free product thicknesses (in excess of approximately 1 inch), the AUTOSKIMMER<sup>R</sup> would be more useful.

The relatively high product thicknesses observed in recovery well 4 and the volume recovered from it led to an investigation of a possible new JP-4 loss. No evidence of such a loss was found, and GC/MS analysis by the Air Force of samples indicated that the JP-4 was aged, not new, and probably from the same source as that found throughout the site (Appendix D). This localized accumulation of free-product JP-4 in and around recovery well 4 appears to have had little or no impact on this study. The fact that no evidence of free product was observed in EA-19, just upgradient of recovery well 4, is evidence that this JP-4 was isolated from most of the site.

##### 2. Nutrient Addition

Restore<sup>R</sup> 375 was added on a batch basis of 150 lb/week and metered into the recirculation flow to make a delivery concentration of 1,000 mg/L. Nutrient solutions were added three times a week, and each pulse was approximately 4 hours. Typically, nutrients were added on Monday, Wednesday, and Friday. In the course of the study 7,800 pounds of Restore<sup>R</sup> 375 was applied. Figure 15 summarizes the application history.

Figure 16 illustrate the distribution of phosphate, ammonia, and chloride on the site over the study duration. Except in upgradient well EA-5, increases in all three parameters can be observed.

To evaluate groundwater travel times on the site and the ability of nutrients to be transported, an initial field transport test was conducted. The results of the nutrient transport test are shown in Figure 17. The transport test was conducted in the following manner: 150 pounds of Restore<sup>R</sup> 375 (see Table 8 for formulation) were dissolved in approximately 100 gallons of tap water, using ARS nutrient-mixing and delivery equipment. The resulting nutrient solution was metered into the injection line to provide an injection concentration of approximately 1,000 mg/L Restore<sup>R</sup>. This concentration of Restore<sup>R</sup> 375 should provide approximately 340 mg/L chloride, 160 mg/L ortho-phosphate, and 160 mg/L ammonia. Injection of nutrients was maintained for a

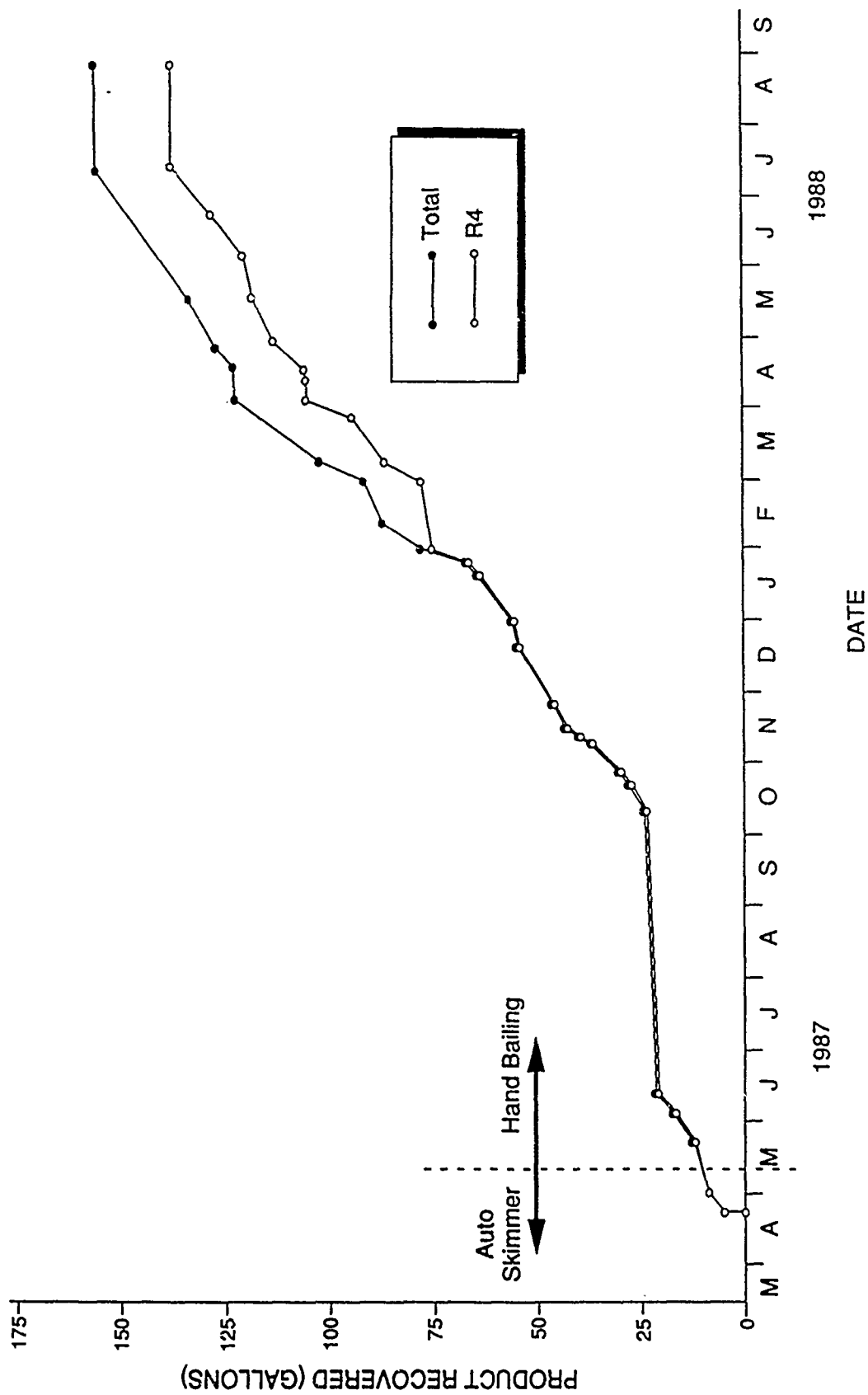


Figure 14. Cumulative History of Free Product Recovery at Eglin POL Demonstration Site.

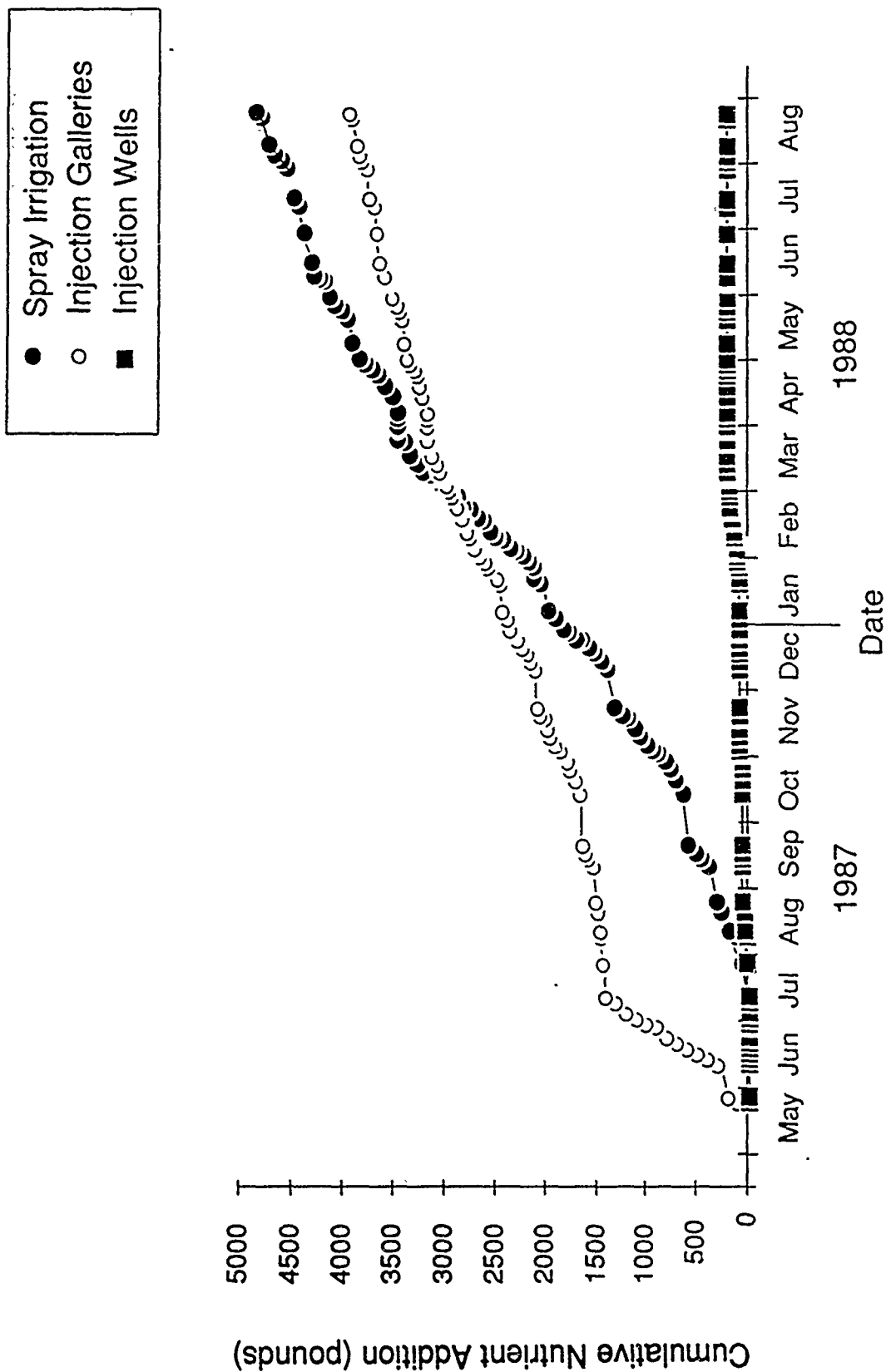


Figure 15. Nutrient Addition History for the Three Application Systems at Eglin POL Demonstration Site.

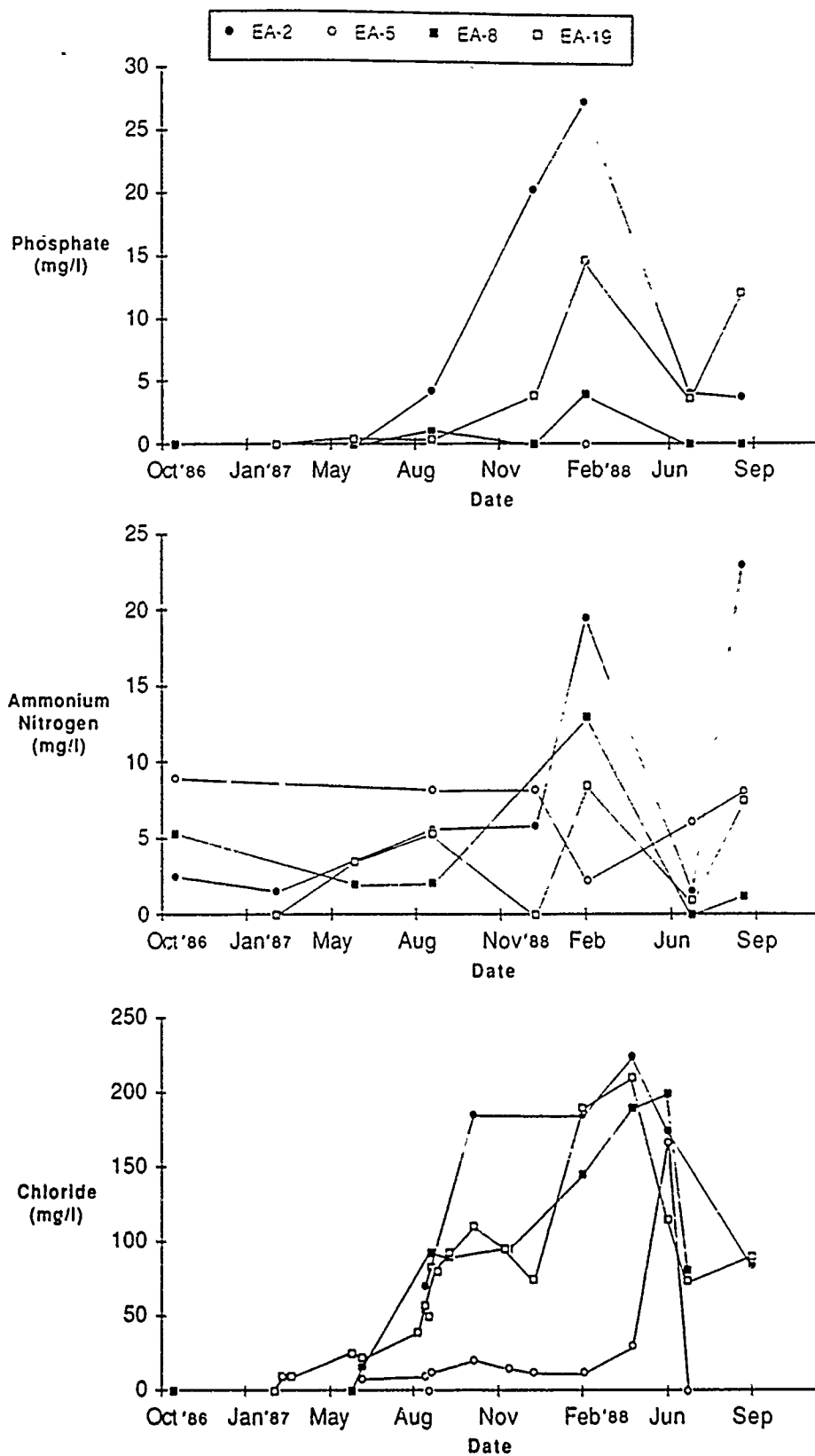


Figure 16. Phosphate, Ammonium Nitrogen, and Chloride Concentrations at Selected Monitoring Wells at the Eglin POL Demonstration Site.

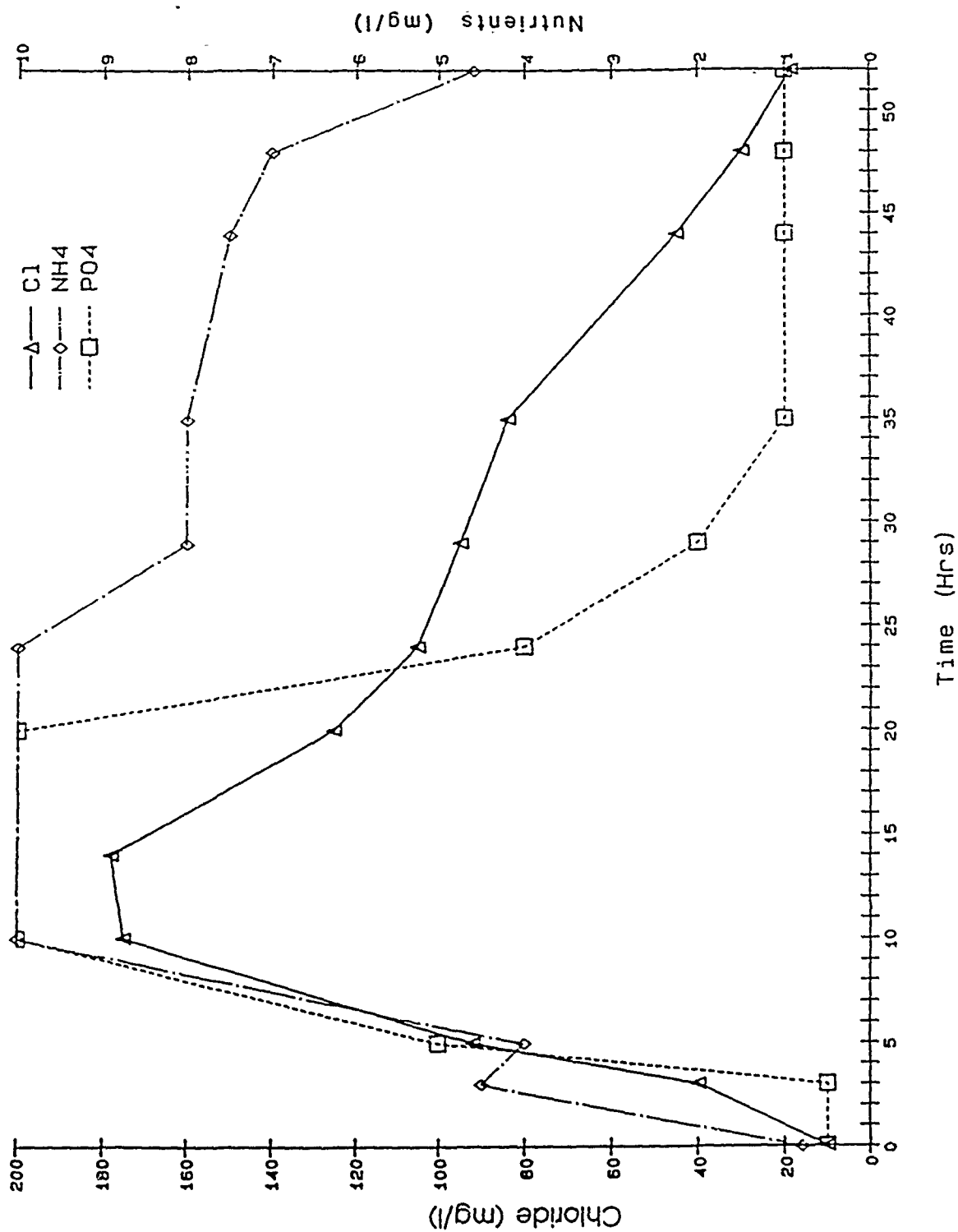


Figure 17. Field Nutrient Transport Test Conducted February 1987 at the Eglin POL Site, Well EA-18.

period of five hours. Primary monitoring points were EA-18, 10 feet down-gradient from the injection gallery, and EA-19, approximately 40 feet down-gradient from the injection gallery. The wells were purged (five casing volumes) prior to sampling.

The figure shows breakthrough of each compound at well EA-18. The highest chloride levels measured were about 50 percent of the theoretical concentration of chloride in the injection water. Injection concentrations of chloride and nutrients were not measured. Ammonia and orthophosphate peaked, at similar concentrations, at about the same time that chloride reached its maximum concentration. Ammonium levels were observed to decrease gradually, whereas the decrease in phosphate was much more precipitous. This finding agrees with the laboratory nutrient test, which indicated somewhat stronger retention of ammonium. The failure of orthophosphate to reach the assumed injection concentration may be due to precipitation losses, but the reasons for the poor recovery of ammonium are unclear.

Well EA-19 was also monitored during the transport test. During the 52-hour test duration, concentrations of chloride, ammonium, and phosphate above background levels were never observed. Samples collected from EA-4 (which is 15 feet north of the injection gallery) analyzed in the laboratory did show elevated concentrations of ammonium (8.0 ppm) and phosphate (0.3 ppm). As shown in Figure 16, elevated phosphate, ammonia, and chloride concentrations were observed in EA-19 after initiation of routine nutrient injections. Ammonium and chloride levels had increased by June 1987; phosphate by January 1988.

### 3. Hydraulic Performance

#### a. Pumping

Groundwater pumping was initiated on February 17, 1987 and ceased for this project after 576 days, on September 15, 1988 (pumping was continued for another AFESC-supported project after that date). A detailed summary of the volumes pumped to the various systems is provided in Appendix E. In the about 20 months of operation, approximately 21.4 million gallons were pumped:

Recovery Well 1	Recovery Well 2	Recovery Well 3	Recovery Well 4
5.2 million	5.8 million	6 million	4.4 million

This is an average yield of 6.5 gpm per well (including down time). In the course of operation, yield of the wells apparently remained constant, with no observed plugging problems.

#### b. Applications

All of the pumped water was reapplied, either via the three main systems or as untreated spray. During the period of pilot testing in the infiltration galleries (February-August 1987), three of the four pumping wells were sprayed untreated (without nutrients or  $H_2O_2$ ) onto the northeastern portion of the site (the area between the infiltration galleries and recovery

wells 3 and 4). Following initiation of full-scale application using infiltration galleries, injection wells and surface spray, the untreated spray application area was limited to the vicinity of EA-8.

The hydraulic performance of each injection system is summarized in Figure 18. The 21.4 million gallons of water extracted were reinjected as follows:

Untreated Spray Area	Spray Irrigation	Infiltration Galleries	Injection Wells
1.5 million	9.9 million	8.9 million	1.1 million

#### (1) Infiltration Galleries

The first four infiltration galleries (GL 1, 2, 3, and 4) were tested and began operating in February 1987. Initially, the four galleries were capable of reinjecting the full design flow of 10 gpm, but after a few weeks of operation their capacity declined to below design, and it was necessary to add three galleries (March 1987: GL 5, 6, and 7). This time the seven combined galleries operated at design flow for a few months, but clogging ensued, and in September 1987 galleries GL 8, 9, 10, and 11 were installed in a gravel trench previously used for free product recovery. After these galleries were installed, flow was maintained to all 11 galleries, and no further plugging problems were encountered. This was most likely due to the large infiltration capacity of the gravel trench, and not to operational changes.

#### (2) Injection Wells

The injection wells were initially tested and operated at the design flow of 5 gpm each. Initial tests indicated that the wells were capable of taking the design flow and substantially more. Shortly after operation, however, the yield fell off sharply. The wells were periodically acid treated with 1 to 2 gallons of 50 percent industrial HCl and vigorously redeveloped using air surge. At first this treatment increased yield, but over time: even with acid cleaning and redevelopment, injection rates fell to the 1 gpm range. There are two probable causes of this clogging: iron precipitation and phosphate precipitation. Oxidized iron precipitation is likely to have caused some of the clogging, but the iron polishing filter should have minimized this problem, and acid washing should have been successful in redissolving much of the iron precipitate. A more likely cause of the long-term problem is a phosphate precipitate, either of calcium or iron. Such a precipitate would be less amenable to acid washing.

It appears that this clogging was limited to the immediate vicinity of the injection wells and did not extend into the aquifer. The result of pump testing in monitoring wells near the injection wells before and after treatment is illustrated below (average transmissivity, gpd/ft):

	February_1987	September_1988
Monitoring well near Inj Well 1	20.200	17.000
Monitoring well near Inj Well 2	15.400	26.800

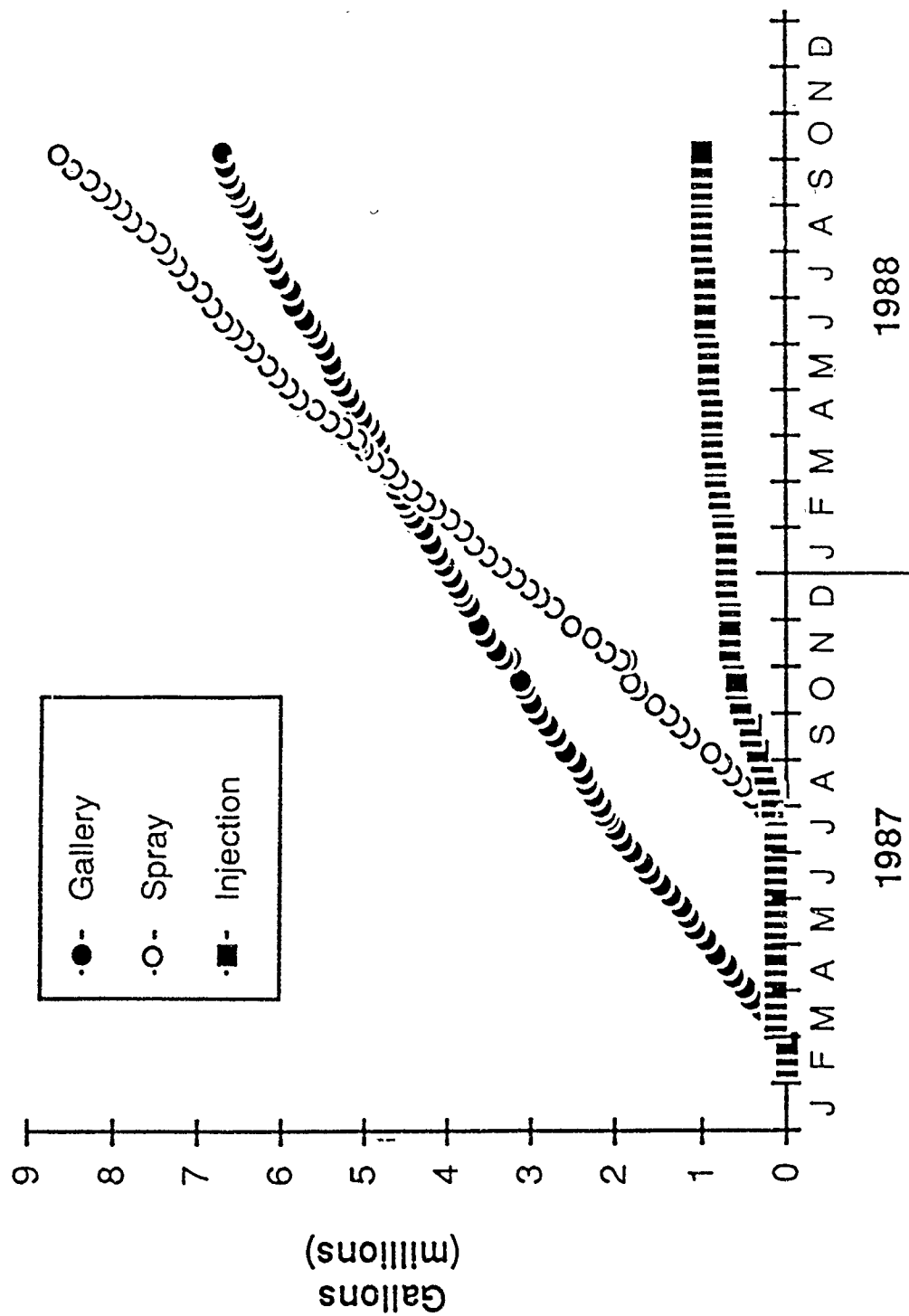


Figure 18. Volume of Water Pumped into the Three Primary Application Systems at the Eglin POL Demonstration Site.

The lack of reduced yield indicates that the formation was not plugged (these yields are based on measured responses in monitoring wells 5-10 feet from the injection wells and not in the injection wells themselves).

### (3) Spray Irrigation

The spray irrigation area easily received the design flow of 10 gpm. The primary problem encountered was vegetative growth. It was necessary to frequently rototill the soil to minimize plant growth. Because the site was located in northern Florida, ice formation was not a problem.

## 4. Aeration/Settling

### a. Iron Removal

The iron removal system was an unexpected addition: the initial site characterization data (Reference 2) had indicated iron levels below 1.0 mg/L. The discovery of higher iron levels led to a field modification of the design to limit iron levels in reinjected water. Although no effort was made to document system performance intensively, data collected on August 29, 1988, should be typical:

	Influent	Sedimentation Basin Effluent	Polishing Filter Effluent
Total Iron (mg/L)	10.2	5.9	2.5

A more efficient clarifier and better-controlled pH adjustment prior to aeration would no doubt improve efficiency. Nonetheless, this low-cost system did successfully remove a significant portion of the iron.

### b. Volatile Organic Removal

The design water flow rate into the aeration basin was 30 gpm, and the air flow rate was 100 cfm, for an average air to water ratio of approximately 25:1. Table 10 illustrates the results of a July 1987 pilot test at three air-to-water ratios ranging from 8:1 to 36:1. These tests indicated that removal of 90 percent or more of the chromatographable organics was possible, and removal of volatiles was much higher. The reduction in TOC, however was approximately 35 percent, about 20 mg/L. The nature of this non-strippable TOC is not known, but it did not consist of chromatographable JP-4 hydrocarbons. Examination of the GC/MS reconstructed ion chromatograms did not show significant unquantified peaks either in the volatile or in the base-, neutral-, and acid-extractable fractions. Table 10 also indicates the efficiency of the aerators at a 25:1 ratio of air to water after more than one year of operation. This high level of efficiency was maintained throughout the project with a minimal maintenance effort. Despite the high iron concentrations and visible iron deposits, the only maintenance necessary was occasional draining of the basin to examine the diffusers and reattach any loose membranes. No cleaning of the iron deposits was required.

TABLE 10. RESULTS OF PILOT TESTING AND OPERATIONAL EFFICIENCY AFTER ONE YEAR OF THE AERATOR SYSTEM AT THE EGLIN POL DEMONSTRATION SITE (mg/L)

	July 1987					August 1988	
	Influent		Effluent			Influent	Effluent <sup>a</sup>
	Beginning <sup>a</sup>	Ending <sup>b</sup>	8.0 <sup>c</sup>	17 <sup>c</sup>	36 <sup>c</sup>		25 <sup>c</sup>
Benzene	0.15	0.18	0.031	0.015	0.008	0.019	<0.002
Toluene	0.38	0.50	0.071	0.033	0.017	0.046	0.002
Ethylbenzene	0.39	0.45	0.062	0.028	0.013	0.12	0.002
m-Xylene	1.2	1.5	0.200	0.087	0.042	0.31	0.003
o+p Xylenes	1.2	0.5	0.240	0.110	0.060	0.53	0.009
2-Methylbutane	0.18	0.20	0.010	0.0036	0.0011	0.10	<0.005
Pentane	0.11	0.098	0.0050	0.0025	0.0012	0.036	<0.005
3-Methyl pentane	0.12	0.14	0.0071	0.0031	0.00076	0.17	<0.005
Hexane	0.076	0.095	0.0041	0.0018	0.0059	0.053	0.006
Methyl cyclohexane	0.17	0.19	0.0013	0.0007	0.0025	0.15	<0.005
3-Methylhexane	0.033	0.041	0.0017	0.00067	0.00029	<0.005	<0.005
Heptane	<0.019	<0.035	0.0023	ND	0.00016	0.034	<0.005
Propylbenzene	0.061	0.072	0.0073	0.0028	ND	0.064	<0.005
3-Ethyl toluene	0.22	0.28	0.033	0.016	0.0074	0.19	<0.005
p-Ethyl toluene	0.23	0.28	0.041	0.019	0.009	0.19	<0.005
1,3,5-Trimethylbenzene	0.14	0.089	0.025	0.011	0.005	0.10	<0.005
1,2,4-Trimethylbenzene	0.49	0.62	0.047	0.035	0.019	0.49	<0.005
2-Butane	-	-	-	-	-	0.031	<0.02
Cyclohexane	-	-	-	-	-	0.13	<0.005
Total Organic Carbon	57	56	37	36	37	18	15

<sup>a</sup>Influent concentrations at the beginning of the pilot test.

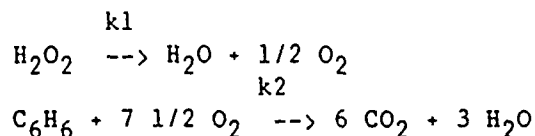
<sup>b</sup>Influent concentrations at the end of the pilot test.

<sup>c</sup>Air to water ratios.

## B. HYDROGEN PEROXIDE AND OXYGEN DELIVERY

Because the JP-4 hydrocarbons are biodegradable under aerobic conditions, the key to success in an enhanced bioreclamation is delivery of sufficient oxygen. The objective is to deliver hydrogen peroxide to the area of active biodegradation, where it will decompose to oxygen at a rate close to the rate of biological oxygen use.

The basic reactions governing peroxide decomposition and subsequent oxygen utilization are:



Where  $k_1$  is the rate of oxygen formation as the result of hydrogen peroxide decomposition and  $k_2$  is the rate of microbial oxygen utilization for hydrocarbon degradation. The stoichiometry of the latter equation depends on the specific hydrocarbon being degraded, in this case benzene.

If  $k_1$  exceeds  $k_2$  oxygen will be released more rapidly than it is being used and oxygen concentrations will increase. When the oxygen concentration exceeds saturation, oxygen will be lost to bubble formation.

### 1. Hydrogen Peroxide Decomposition

In practice, hydrogen peroxide is frequently added in increasing doses, beginning at levels of approximately 100 mg/L gradually increasing to the design concentration. Phosphate addition is typically initiated prior to hydrogen peroxide, in an effort to reduce hydrogen peroxide decomposition rates.

As shown in Figure 19, in this study hydrogen peroxide injection concentrations were initiated at 100± mg/L and gradually increased to the design level of 500± mg/L.

#### a. In-Situ Decomposition Observations

Following the increase to 500± mg/L, groundwater was observed to be mounded to the ground surface, and bubbles were observed rising through the soil overlying the galleries. This, combined with the observation that no hydrogen peroxide could be detected in any monitoring wells, led to the suspicion that the hydrogen peroxide was decomposing very rapidly, resulting in offgassing.

In order to determine the rate of hydrogen peroxide decomposition and biological oxygen use, in-situ wells were installed within and very close to the gallery areas. A series of shutdown tests were then conducted: in these tests hydrogen peroxide rates are held steady until steady-state hydrogen peroxide and oxygen concentrations are reached in the wells of interest. The flow is then shut down and hydrogen peroxide and/or oxygen levels are monitored over time to determine in situ decay rates. The results of the shutdown tests indicated that the hydrogen peroxide decomposition rates were quite rapid.

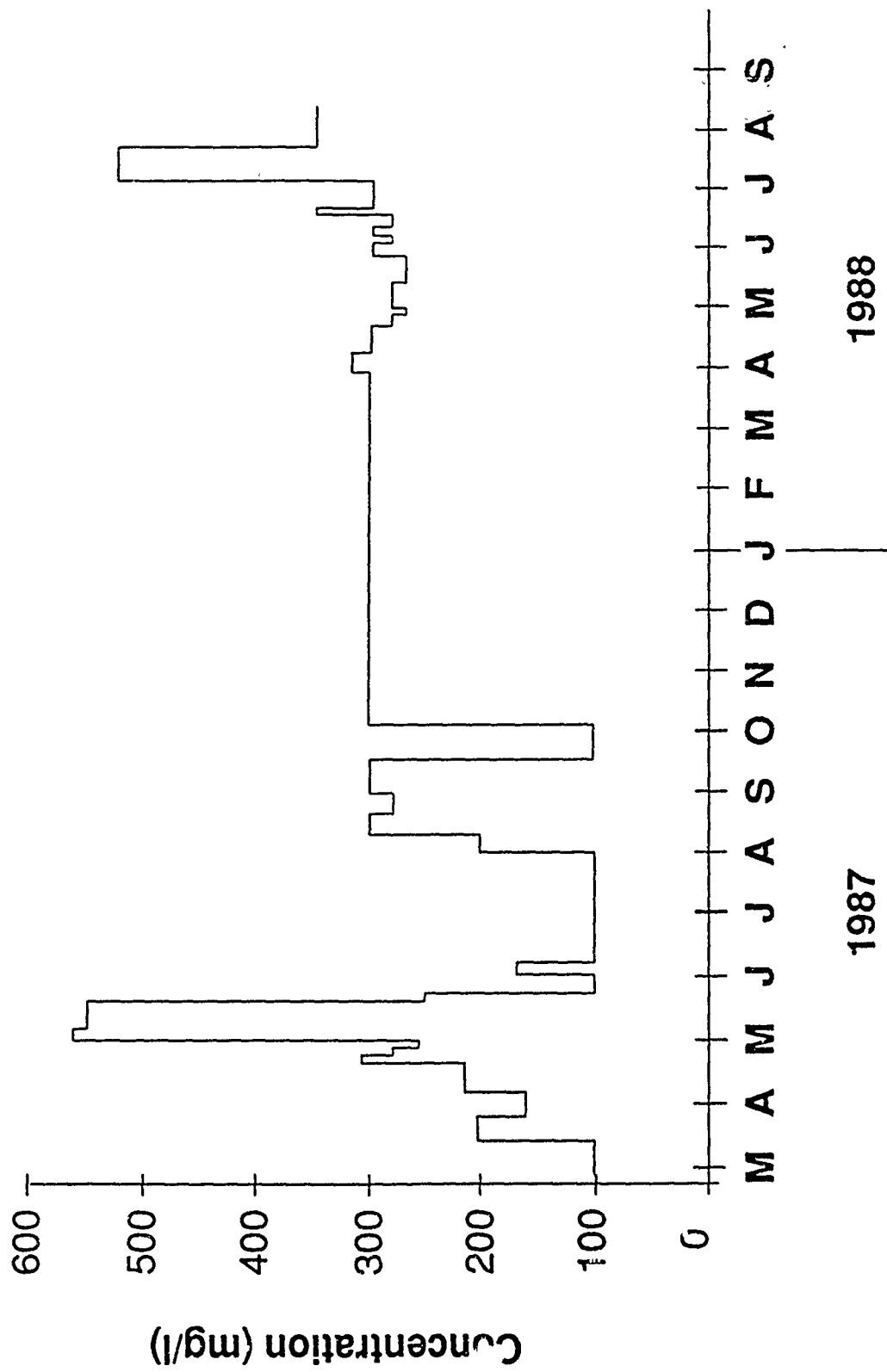


Figure 19. Hydrogen Peroxide Concentration in Injection Systems at the Eglin POL Demonstration Site.

Gas samples were collected from the bubbles observed on the infiltration galleries and analyzed for major gases. The results, illustrated in Table 11, indicate that these bubbles do consist primarily of oxygen, well above the levels found in ambient air. This further supports the conclusion that much of the hydrogen peroxide was decomposing and being lost as offgas.

These observations led to several operational changes. When the new galleries, GL 8, 9, 10, and 11 were added, they were pretreated with the Restore<sup>R</sup> 375 nutrient solution in an effort to reduce hydrogen peroxide decomposition rates. This did not lead to significantly improved hydrogen peroxide stability.

The Air Force conducted a series of in-house laboratory tests, described by Reference 24, which indicated that the primary cause of this decomposition was microbially produced enzymes. This finding led to an effort to increase peroxide stability through shocking the infiltration galleries with elevated levels of hydrogen peroxide. The infiltration galleries were shocked with 3,500 mg/L of peroxide on three occasions, but no lasting improvement on hydrogen peroxide stability was noted. Another potential method of reducing bacterial enzyme activity was to limit the available carbon in the galleries and starve the bacteria. Carbon-free tap water was used in the following experiments to create this effect.

#### b. Experimental Galleries for Peroxide Stability Tests

The peroxide stability observations raised several questions which were addressed by the construction of five smaller-scale infiltration galleries for more controlled operation. The location of these galleries are indicated in Figure 20. Figure 21 illustrates the construction detail of EGL 1, 2, 3, and 4. These galleries were approximately 5 feet long. EGL 5 was installed in a square pit approximately 5 feet x 5 feet. It was excavated to groundwater, and backfilled with gravel after a plastic liner had been placed on the trench side walls. This was to ensure that water injected into EGL 5 did not pass through the vadose zone. Well EA-40 was installed in EGL 5.

Five treatments were used to evaluate the effect of various operating perimeters on peroxide stability and oxygen utilization:

- EGL-1 Clean (carbon free) water
- EGL-2 Clean water, soils pretreatment with Restore<sup>R</sup> 375
- EGL-3 System water, soils pretreatment with Restore<sup>R</sup> 375
- EGL-4 System water
- EGL-5 System water, injected to saturated zone only

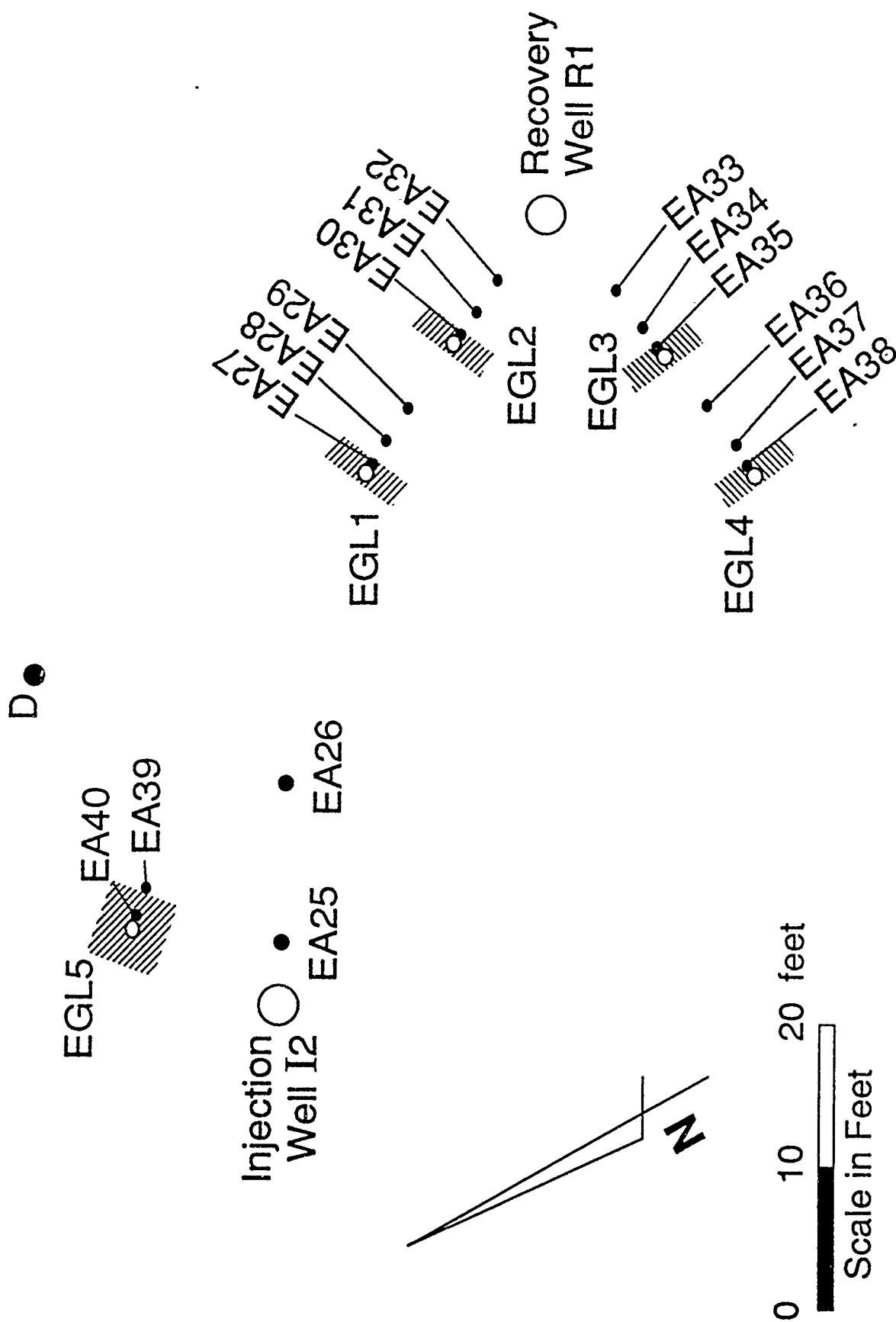


Figure 20. Layout of Experimental Galleries at the Eglin POL Demonstration Site.

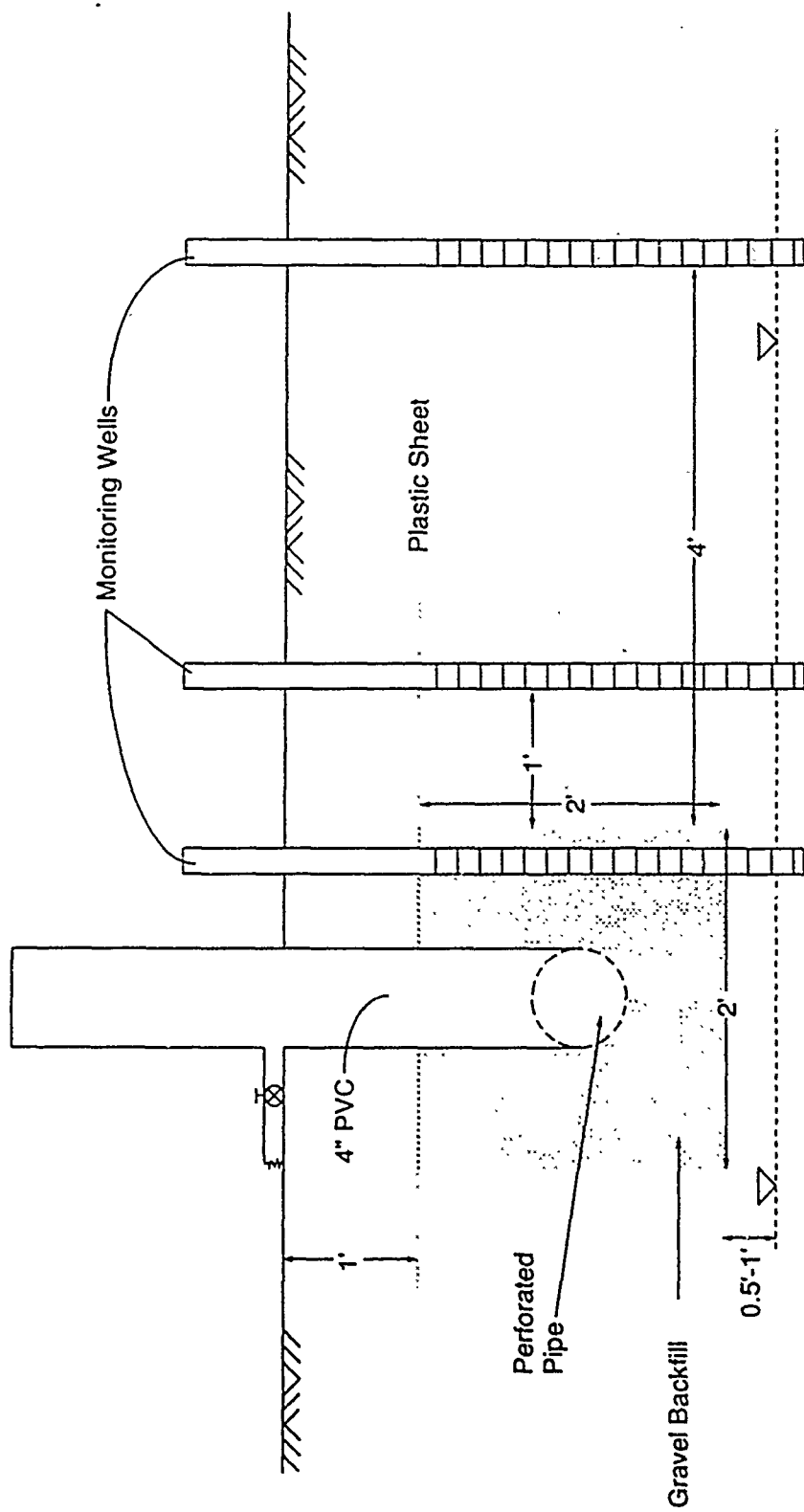


Figure 21. Typical Cross-Section Detail of Experimental Galleries.

Clean water consisted of tapwater passed through a 55-gallon activated carbon cylinder, and system water was treated groundwater taken from the treatment system. The two different water supplies are compared in Table 12.

The design flow to enter each gallery was 2 gpm. Soils pretreatment consisted of injecting Restore<sup>R</sup> 375 at each gallery before initiating peroxide injection. The objective was, under normal operating conditions, to maintain peroxide concentrations at approximately 300 mg/L, allow acclimation to occur, and then introduce a shock of 5,000 mg/L for a 24-hour period. Periodically, shutdown tests were run in which flow was stopped and peroxide and oxygen

TABLE 11. RESULTS OF ANALYSIS OF OFF GAS COLLECTED FROM  
SELECTED INFILTRATION GALLERIES

	Sample			
	GL-2	GL-6	GL-9	Background ---(air)---
Oxygen	82.0%	83.0%	36.0%	21%
Nitrogen	16.0%	16.0%	59.0%	78%
Carbon Dioxide	1.5%	1.0%	5.4%	<1.0%
Methane	<0.2%	<0.2%	<0.2%	<1.0%

concentrations were measured. Figure 22 shows the results of one shutdown test; more than 400 similar tests were run. This is a typical result, in which the peroxide decayed rapidly: the oxygen remained saturated until the peroxide was gone and then slowly decayed. In these tests generally there was an order of magnitude or more difference between the peroxide decomposition rate ( $k_1$ ) and the oxygen utilization rate ( $k_2$ ).

In addition to the various water and nutrient treatments, a shock of 5,000 mg/L of hydrogen peroxide was attempted. No significant difference was noted between the treatments. Pretreatment had little effect on stability. The only apparent difference was in response to the 5,000 mg/L shock in the galleries receiving clean water. Peroxide stability was briefly increased, but only in the immediate vicinity of the gallery and the effect was very temporary.

TABLE 12. CHEMICAL CHARACTERISTICS OF INJECTION WATERS UTILIZED FOR THE  
 EXPERIMENTAL GALLERY TESTS, EGLIN AFB ENHANCED BIORECLAMATION  
 DEMONSTRATION (mg/L)

	<u>Clean Water</u>	<u>System Water</u>
Total Iron	<0.03	2.8
Total Aluminum	0.09	<0.1
Total Manganese	15.4	2.3
Total Manganese	<0.02	0.079
Total Sodium	14	49
Calcium	24	19
Alkalinity	120	28
Chloride	5.1	75
Fluoride	0.3	<0.1
Inorganic Carbon	30.7	10.8
Filterable Residue	150	220
Total Organic Carbon	<1	15

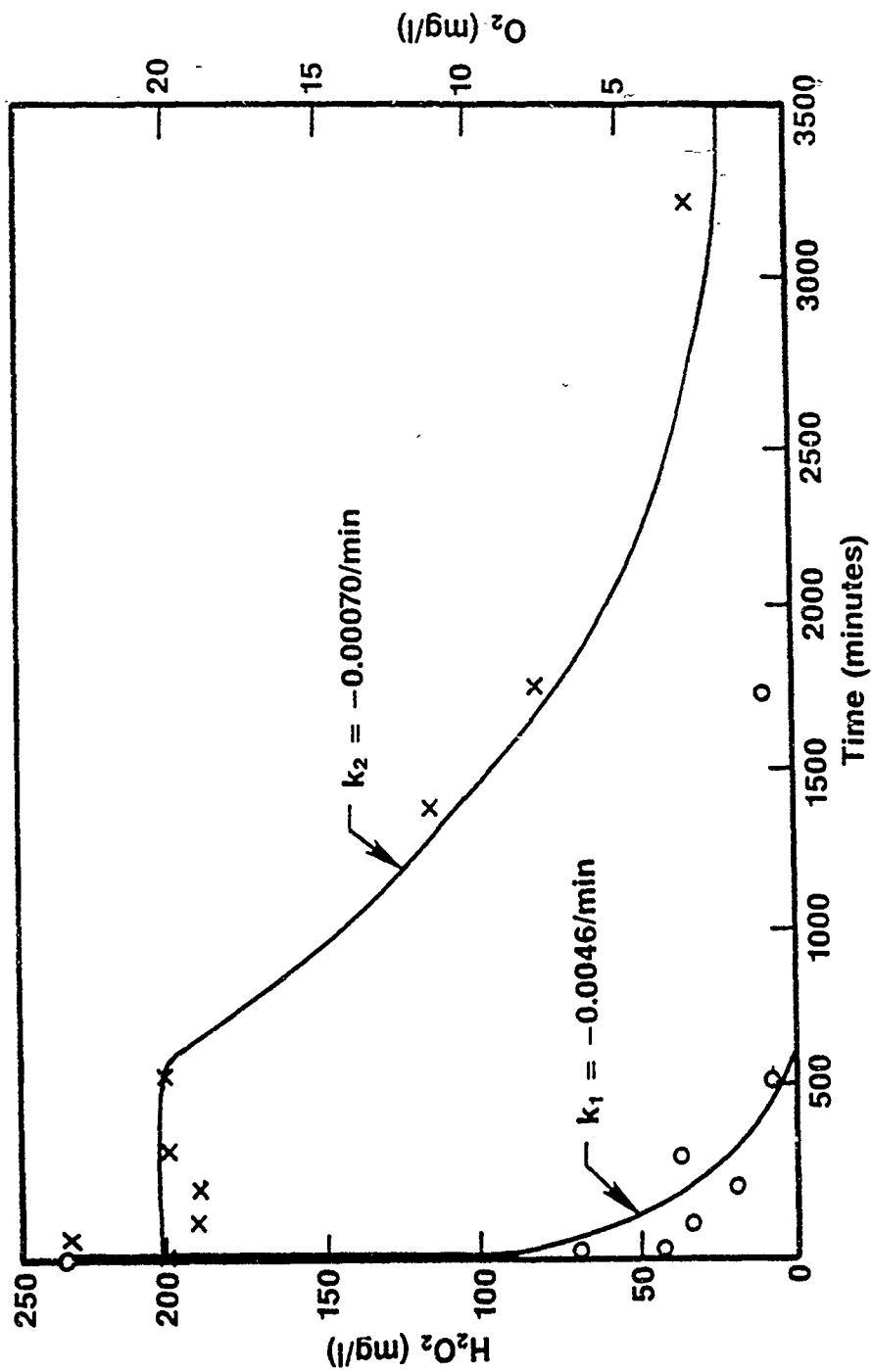


Figure 22. Results of a June 15, 1988, Shutdown Test of EGL-1, EA-27.

This hydrogen peroxide instability is no doubt due to a variety of causes. Spain et al. found that the rapid decomposition at the Eglin test site is due to biological enzyme activity promoted by aerobic microorganisms at the point of injection. It is apparent, however, that phosphate pretreatment, use of clean injection water and peroxide shocking are not sufficient to overcome inorganic or enzymatic catalysis and significantly extend the peroxide half-life.

#### c. Peroxide Use Efficiency

Based on the shut down tests, an estimate can be made of the hydrogen peroxide use efficiency at the Eglin POL demonstration site. The rate of this oxygen loss may be estimated by simplifying the equation and applying it to any single point in the aquifer:

$$\frac{dO_2}{dt} = k_1 H_2O_2 - k_2 O_2$$

where

$$O_2^2 = \text{oxygen loss to bubble formation}$$

As this will only occur when oxygen levels become saturated, the oxygen concentration may be assumed to be a constant equal to saturation. Rearranging terms, one may solve for the oxygen utilization efficiency at this given point as follows:

$$E = \frac{k_2 C_2}{k_1 H_2O_2} \times 100$$

where

E = oxygen utilization efficiency (percentage of oxygen delivered that is biologically utilized).

Estimates of the terms necessary to calculate use efficiency may be made either from existing literature or field observations at the Eglin AFB, demonstration site. The peroxide decomposition rates observed at the demonstration

site under normal operating conditions ranged from approximately 0.1 to 0.01 minute<sup>-1</sup> (7 to 90-minute half lives.) Watts (Reference 27) found a peroxide decomposition rate of approximately 0.01 minute<sup>-1</sup> in a sandy loam soil. Lawes (Reference 26) found the Eglin POL Demonstration Site soils to have a lower rate of peroxide decomposition than several other sandy soils. Therefore, it is reasonable to assume that the 0.1 to 0.01 minute<sup>-1</sup> range is realistic for onsite peroxide decomposition rates.

Oxygen use rates are more difficult to estimate. Field observations at the Eglin POL Demonstration site have generally indicated a range of 0.001 minute<sup>-1</sup> to 0.0001 minute<sup>-1</sup>. Very few observations of in-situ oxygen use rates have been made, however Metcalf and Eddy (Reference 28) reported typical activated sludge substrate use rate of 0.007 minute<sup>-1</sup> to 0.001 minute<sup>-1</sup>. Although Metcalf and Eddy's observations are for a suspended growth system for sewage, and not for petroleum hydrocarbons, their results do indicate that the Eglin rates are in the same range as other carbon-rich aerobic biological systems.

Oxygen saturation in groundwater is primarily a function of the partial pressure of oxygen in the gas in contact with the water. Assuming a 100 percent oxygen atmosphere at one atmosphere of pressure, approximately 40 mg/L of oxygen would constitute saturation. At Eglin AFB, the maximum observed oxygen concentrations (those found in the presence of rapidly decomposing peroxide) were on the order of 20 to 30 mg/L.

We may now solve the equation for selected cases. Using a hydrogen peroxide concentration of 300 mg/L, the simplest best and worst cases are as follows:

	$k_1$	$k_2$	$O_2$	E
Best case	0.01 minute <sup>-1</sup>	0.001 minute <sup>-1</sup>	40 mg/L	13%
Worst case	0.01 minute <sup>-1</sup>	0.00001 minute <sup>-1</sup>	20 mg/L	$6.7 \times 10^{-5}\%$

Even if in the best case, an order-of-magnitude improvement in hydrogen peroxide stability (to 0.001 minute<sup>-1</sup>) is assumed, only 13 percent of the available oxygen is used for microbiological respiration and the remaining 87 percent is lost to bubble formation.

These estimates are for the peroxide present at a given point, and not necessarily applicable to the applied peroxide. Some hydrogen peroxide is used to increase the oxygen concentration from 8 to 30 mg/L (approximately 44 mg/L of H<sub>2</sub>O<sub>2</sub>), so using the best-case estimate approximately 48 mg/L, or 16 percent, of the delivered hydrogen peroxide was used for biodegradation.

In an effort to determine whether any of the gaseous oxygen from hydrogen peroxide was being used for biodegradation in the unsaturated zone, soil gas samples were collected for carbon dioxide and oxygen analysis. An effort was made to collect samples from a background location and from locations within the treatment zone both close to injection points and at a distance from these points. It can be assumed that if the sum of the oxygen and carbon dioxide concentrations exceed 21± percent, we are seeing a source of oxygen which is greater than atmospheric (20.9% in air and 8± mg/L in water). The results of these analyses (Table 13) do not suggest the presence of elevated levels of

TABLE 13. OXYGEN AND CARBON DIOXIDE CONCENTRATIONS IN SOIL GAS AT THE EGLIN  
FOL DEMONSTRATION SITE (percent)

<u>Location</u>	<u>Depth (feet)</u>	<u>March 1988</u>		<u>August 1988</u>	
		<u>Oxygen</u>	<u>Carbon Dioxide</u>	<u>Oxygen</u>	<u>Carbon Dioxide</u>
EA4	1	17.3	1.5	20.3	0.75
	2	5.3	8	14.4	3.2
	3	20.8	0.04	1.7	10
	4	20.6	0.05	-	-
EA5	1	7.7	12	19.1	1
	2	1.6	15.5	16.1	4
	3	0.4	10	8.8	12
EA6	1	20.8	0.4	20.5	0.1
	2	-	-	19.8	0.23
	3	-	-	20.2	0.15
EA8	1	14.9	4	20.5	0.2
	2	13	5	11.2	2
	3	12.6	3.5	10.2	2
EA25	1	20.8	1.7	20.9	0.1
	2	20.6	3	20.5	0.1
	3	20	4.4	20.3	0.1
	4	20.6	1.8	19.1	1
Background Air	-	20.9	0.1	20.9	0.05

oxygen (or carbon dioxide) as the result of hydrogen peroxide decomposition. This is most likely due to the rapid decomposition of  $H_2O_2$  and the high water table near the injection points.

Although the authors are not aware of other in-situ peroxide stability or similar oxygen in-situ use studies, these observations are not inconsistent with other published field studies. In the American Petroleum Institute's Granger study (Reference 29) and the U.S. Air Force Kelly AFB study (Reference 1), no hydrogen peroxide was detected in any downgradient monitoring well.

#### d. Hydrogen Peroxide Stability in the Injection Wells and the Spray Irrigation Area

No hydrogen peroxide was ever observed in any well in the spray irrigation area or in any well influenced by the injection wells (with the exception of EA-25, which is less than one foot from Injection Well 2).

A lysimeter was constructed to permit the collection of infiltrate at various depths in the spray irrigation area (Figure 23). The results of oxygen and peroxide analysis are presented in Table 14. Oxygen profiles with depth were not always consistent, but several conclusions are apparent. Sampling of surface puddles showed the hydrogen peroxide was not lost to volatilization or in the spray. It appears however that the hydrogen peroxide decomposed in the uppermost six inches of soil.

## 2. Oxygen Distribution History

The distribution of oxygen at selected monitoring wells and in the recovery well discharge is illustrated in Table 15. Only in wells very close to injection points did dissolved oxygen levels increase significantly, and in those wells the oxygen disappeared rapidly after the termination of peroxide injection. It does not appear that application of the hydrogen peroxide had a measurable effect on oxygen levels beyond the immediate injection points. This conclusion is compatible with the observations of hydrogen peroxide decomposition and biological oxygen use rates. Most of the oxygen appears to have been lost as offgas, and what did become dissolved in water was used for biological activity.

## C. MICROBIAL BEHAVIOR

Soil and groundwater samples were collected throughout the project for microbial enumerations.

The results of the enumeration of bacteria in the soil (Figure 24) show densities that generally ranged from  $10^4$  to  $10^6$  colony-forming units (CFU) per gram for total bacteria and for hydrocarbon degraders. There appears to be no relation of total bacterial density to sampling depth: at some locations higher numbers of bacteria were recovered in the zone 6 to 12 inches above the water table, while in other cases the greater densities were found below the water table. Likewise, the densities of hydrocarbon-degrading bacteria in the soils do not appear to be related to sampling depth. No clear increase in bacterial density appeared in the course of the study.

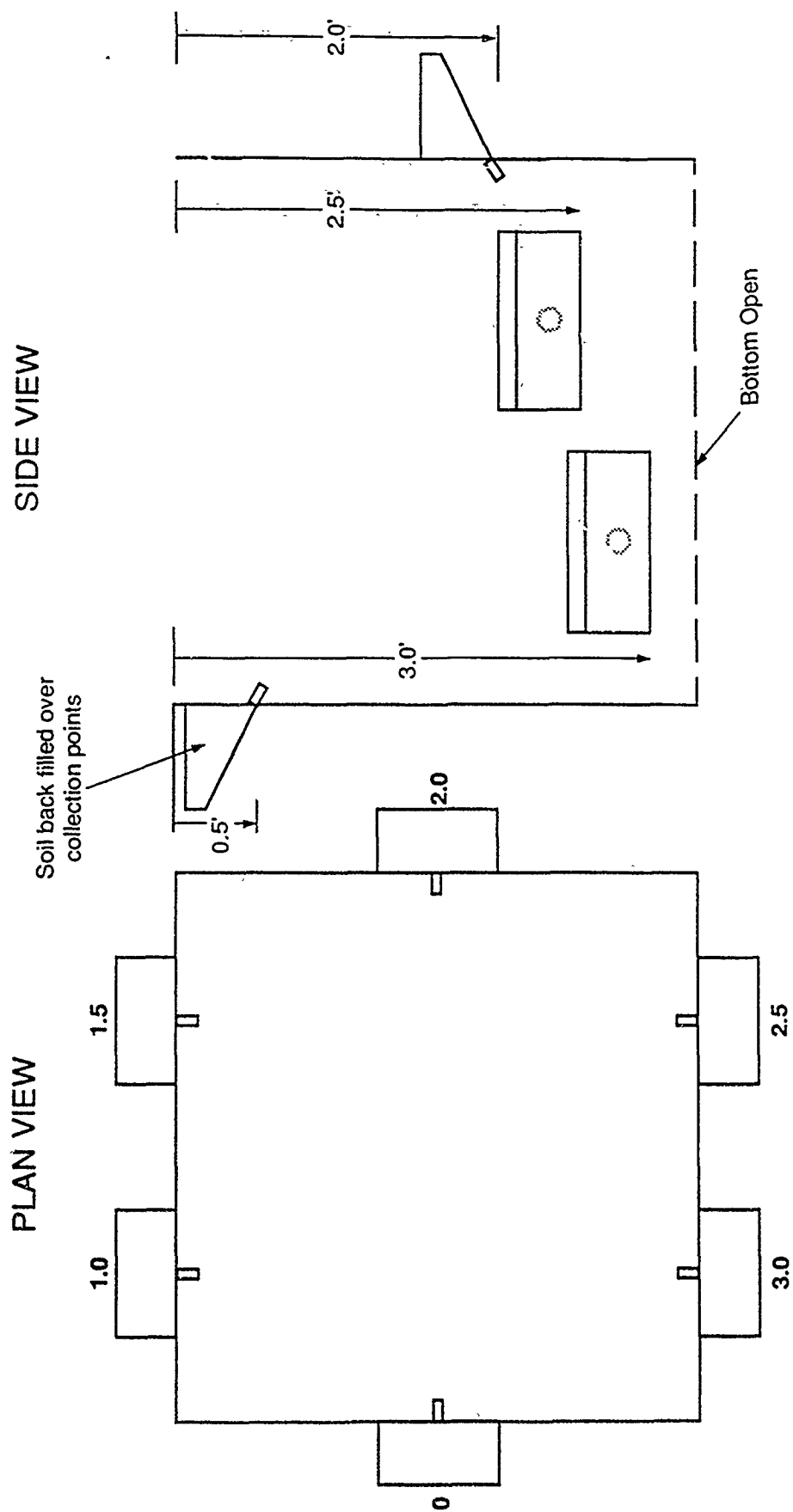


Figure 23. Lysimeter Construction Details.

TABLE 14. RESULTS OF LYSIMETER TESTING IN THE  
SPRAY IRRIGATION AREA (mg/L)

Sample	5/10/88		5/23/88		8/12/88	
	H <sub>2</sub> O <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	O <sub>2</sub>
In-line <sup>a</sup>	270	16	270	19	300	-
Spray <sup>b</sup>	270	16	270	16	-	-
0 ft BLS <sup>c</sup>	96	23	270	17	-	-
0.5 ft BLS	ND <sup>d</sup>	3.4	ND	5.2	ND	3.6
1.0 ft BLS	ND	3.7	ND	5.3	ND	4.1
1.5 ft BLS	ND	2.7	ND	3.4	ND	3.6
2.0 ft BLS	ND	4.2	ND	3.3	-	-
2.5 ft BLS	ND	2.1	ND	3.5	-	-

<sup>a</sup>In-line refers to the feed concentrations in the water lines feeding the spray irrigation area.

<sup>b</sup>Spray refers to samples collected in a glass beaker placed on the ground and allow to fill with spray.

<sup>c</sup>Sample depths refer to feet below land surface (BLS), the 0 ft BLS sample was collected from pooled water on the ground surface.

<sup>d</sup>ND means not detected, detection limits were 1± mg/L.

TABLE 15. OXYGEN CONCENTRATIONS (mg/L) IN SELECT MONITORING WELLS AT THE EGLIN  
POL DEMONSTRATION SITE

Well	1987										1988			
	3-13	4-17	5-28	6-9	6-30	9-8	11-30	12-3	4-28	6-10	8-26	9-14		
EA1	0.6	2.8	2.8	1.8	-	-	-	-	-	-	-	-	-	-
EA2	0.4	2	1.9	1.2	-	1.8	-	-	3.2	1.7	1	2.1	-	-
EA3	0.5	1.3	1.7	1.6	1.2	1.6	-	1.6	1.5	2.1	1.1	1.3	-	-
EA4	0.6	1.2	2.6	1.4	-	1.7	-	-	2	1.7	1.1	1.3	-	-
EA5	0.5	1.8	1.6	2.4	-	1.8	-	2.2	1.8	2.8	-	-	-	-
EA6	2	1.9	2.3	2	-	1.4	-	1.4	1.9	2	-	-	-	-
EA7	0.5	1.8	3	1.4	-	1.4	-	-	1.7	3.1	-	-	-	-
EA8	0.6	2.4	1.6	1.2	0.9	1.4	-	1.6	1.8	1.8	-	0.8	-	-
EA9	-	-	-	-	1.1	2.1	-	1.5	2.5	1.8	-	-	-	-
EA10	-	-	-	-	1.2	-	-	-	-	-	3	2.8	-	-
EA13	-	-	-	-	1	1.8	-	1.3	1.4	1.6	1	1.4	-	-
EA14	-	-	-	-	1.4	-	-	-	-	-	-	-	-	-
EA15	-	-	-	-	1.3	1.6	-	-	1.9	1.8	-	-	-	-
EA18	1	2.1	-	2	1.2	1.6	-	1.8	2.2	2	-	-	-	-
EA19	1	1.1	2	1.4	2.1	1.5	1.8	1.4	1.5	1.6	1.4	1.4	-	-
EA20	0.4	-	-	-	1.3	1.8	-	1.1	1	1.4	-	-	-	-
EA21	-	-	2.6	1.9	-	1.8	-	1.6	2.2	2.3	1.8	1	-	-
EA23	-	-	-	-	-	3.5	3.4	-	-	-	3.3	-	-	-
EA24	-	-	-	-	-	-	-	-	-	-	7.7	1.3	-	-
EA25	-	-	-	-	-	1.8	-	-	1.2	9	-	-	-	-
EA26	-	-	-	-	-	1.9	-	-	1	1.5	-	-	-	-
R1	-	-	-	-	0.8	0.6	1.2	0.9	-	-	-	0.8	-	-
R2	-	-	-	1.4	0.8	0.6	-	0.8	0.9	-	-	0.5	-	-
R3	-	-	1.9	-	1.4	0.6	-	0.7	0.8	-	-	0.6	-	-
R4	-	-	-	-	0.9	0.6	-	0.6	0.9	-	-	0.6	-	-

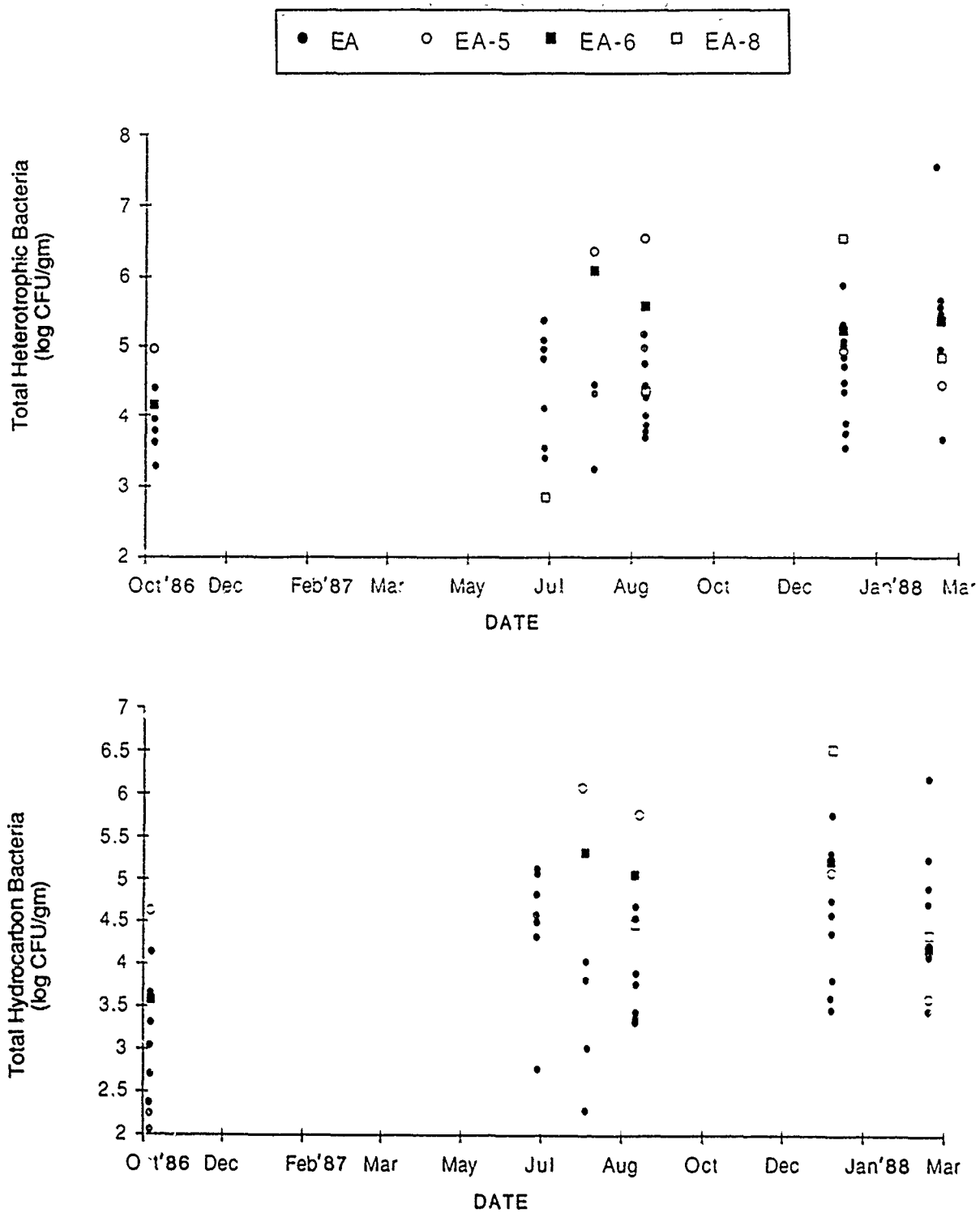


Figure 24. Total Heterotrophic and Hydrocarbon-Degrading Bacteria in Soil from the Eglin POL Demonstration Site.

Enumeration of the groundwater samples (Figure 25), again revealed total bacterial populations and hydrocarbon-degrading bacteria, with densities generally ranging between  $10^5$  and  $10^6$  CFU per ml. As with soils, no clear increase is apparent over the life of the study.

#### D. CONTAMINANT BEHAVIOR

Chemical characterization of the JP-4 contaminant behavior consisted of: an initial intensive sampling which was used both to develop a baseline for further sampling and to develop protocols for subsequent sampling and analysis; periodic ongoing sampling and analysis to document progress; and a final intensive sampling and analysis at the program's completion. The analysis consisted of TPH and TOC to represent gross hydrocarbon contamination in soil and groundwater, respectively, and a GC/MS analysis to identify and quantify individual JP-4 constituents. Analytical methods are described in Section II D.

##### 1. Groundwater

As indicated in Table 16 and Figure 26, TOC showed a general decline in concentration when compared to the contaminated control, EA-5. Examination of trends in the specific chemical constituent analysis data (Table 17) does indicate reduced concentrations of the more soluble aromatic fraction. Figure 27 indicates a general decline of the aromatics in all but the untreated control area, well EA-5. This is in contrast to the aliphatics, represented by hexane, octane, and nonane, which shows no discernible trend over the project life. This is probably due to the higher relative solubility of the aromatics and the flushing action of pumping water through the site. Assuming a treatment area of 22,000 ft<sup>2</sup>, an average saturated thickness of 5 feet (within the treatment area), and a porosity of 0.35, the 21,400,000 gallons pumped represents approximately 75 pore volumes. It is expected that this would result in substantial soil flushing, with significant dissolution of the more soluble JP-4 fraction. It should be noted, however, as discussed in the next section, that similar losses of the aromatic fraction were not observed in the soils, indicating that the decline in groundwater concentrations may be temporary.

##### 2. Soils

As indicated in Tables 18 and 19, no clear trends in either total hydrocarbons or individual JP-4 constituents in the soil were apparent. This is equally true in all portions of the site. In the spray irrigation area approximately 9,900,000 gallons of water were applied to 4,000 ft<sup>3</sup> of soil. Assuming an average vadose zone thickness of 5 feet, and a porosity of 0.35, an estimated 190 pore volumes of water passed through this area. The lack of substantial hydrocarbon removal indicates not only that biodegradation was not an effective cleanup mechanism, but also that soil flushing was not.

The fact that soil flushing did not clean these soils is supported by the GC/MS data. If good contact was made between the residual JP-4 in the soils and the flushing water, it would be expected that the more-soluble aromatic fraction would have been removed selectively. This was not the case with the soils: GC/MS data collected from soil samples at EA-2, in the spray irrigation area, indicate very little change in the aromatic concentrations. The

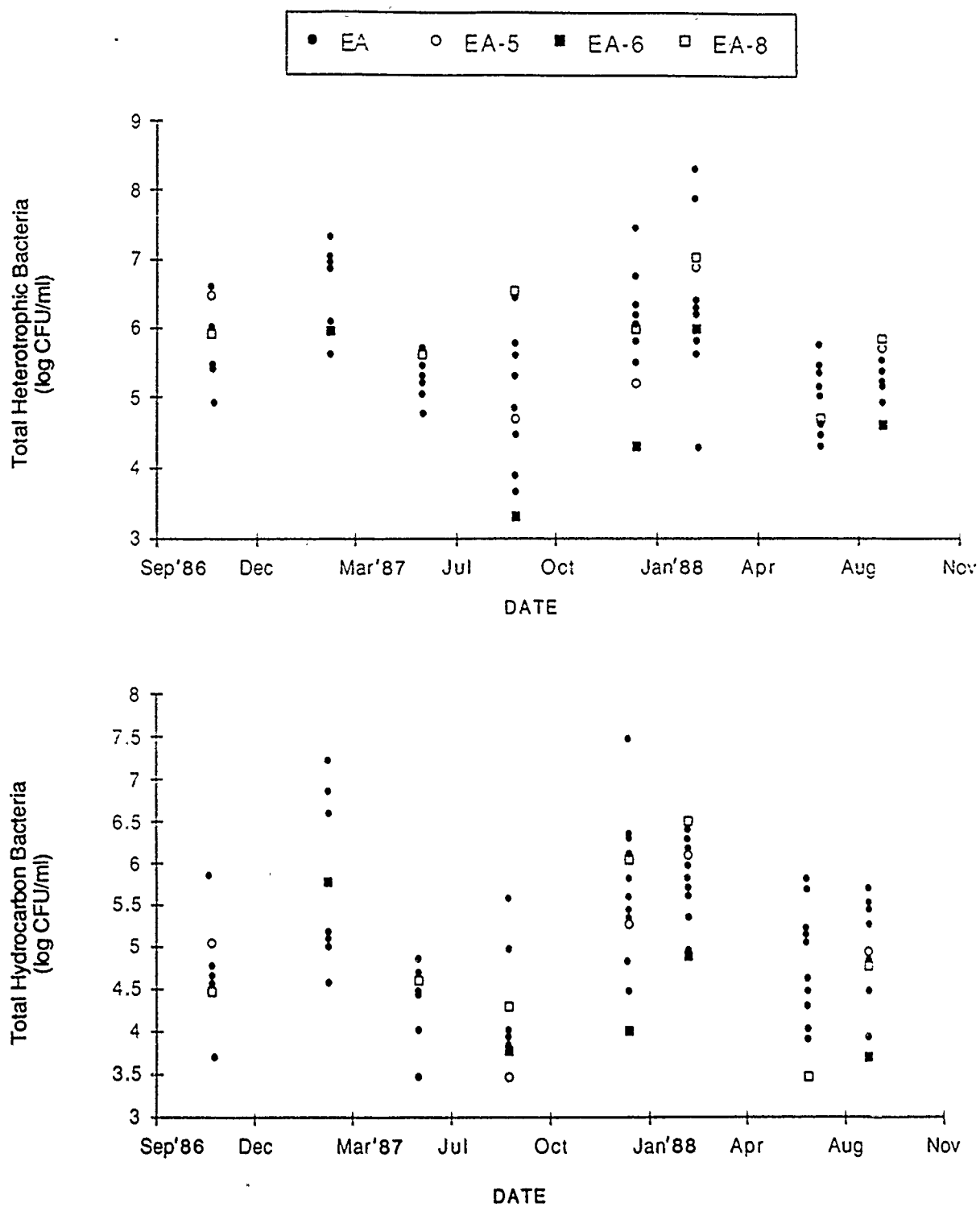


Figure 25. Total Heterotrophic and Hydrocarbon-Degrading Bacteria in Groundwater from the Eglin POL Demonstration Site.

TABLE 16. TOTAL ORGANIC CARBON CONCENTRATIONS IN GROUND WATER AT THE EGLIN POL DEMONSTRATION SITE

<u>Location</u>	<u>TOC 11/86</u>	<u>TOC 03/87</u>	<u>TOC 07/87</u>	<u>TOC 09/87</u>	<u>TOC 01/88</u>	<u>TOC 03/88</u>	<u>TOC 08/88</u>
B	10	-	-	-	-	-	11.0
EA1	317	40.9	29.0	31.0	49.0	13.5	-
EA2	49	-	49.0	46.0	61.0	16.2	26.0
EA3	206	-	49.0	53.0	48.0	38.9	18.0
EA4	198	-	127.0	127.0	38.0	57.9	18.0
EA5	218	-	157.0	215.0	239.0	73.7	110.0
EA6	-	14.5	15.0	15.0	45.0	8.1	14.0
EA7	92	-	63.0	51.0	66.0	36.9	59.0
EA8	122	-	73.0	74.0	58.0	32.4	16.0
EA18	-	-	58.0	50.0	62.0	27.4	13.0
EA19	-	84.5	132.0	56.0	43.0	14.9	21.0

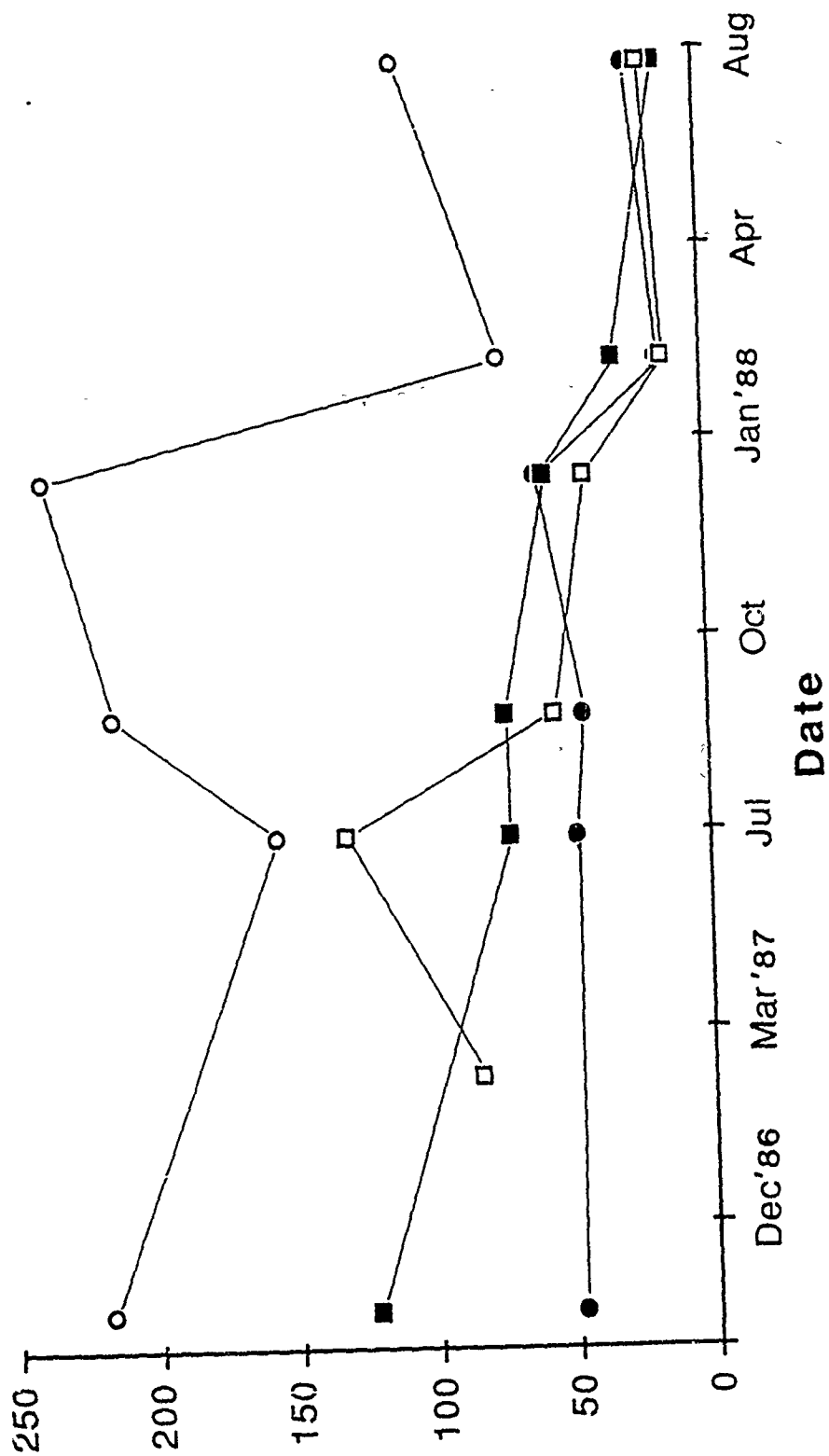


Figure 26. Total Organic Carbon (mg/L) in Selected Monitoring Wells at the Eglin POL Demonstration Site.

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE (mg/L)  
NOVEMBER 1986 AND AUGUST 1988

Compound	EA1		Compound	EA1	
	11/86	08/88		11/86	08/88
Benzene	1.200	0.020	Benzo(a)anthracene	<0.01	NA
Toluene	0.099	0.081	Crysene	<0.01	NA
Ethylbenzene	0.640	0.103	Benzo(b+k)fluoranthene	<0.02	NA
m-Xylene	2.606	0.440	Phenol	<0.01	NA
o-p Xylenes	1.300	0.870	2,4-Dimethylphenol	0.019	NA
2-Methylbutane	0.071	<0.005	2-Methylphenol	NQ	NA
Pentane	0.057	<0.005	4-Methylphenol	NQ	NA
Cyclohexane	0.330	0.021	Benzoic acid	NQ	NA
3-Methylpentane	NA	0.006	2-Methylnaphthalene	0.034	NA
Hexane	NQ	0.005	1-Methylnaphthalene	0.049	NA
Methylcyclohexane	NQ	0.017	2,6-Dimethylphenol	NQ	NA
3-Methylhexane	NQ	0.005	Octanol	NA	NA
Heptane	NQ	<0.005	2,4-Dimethylbenzoic acid	NA	NA
Propylbenzene	0.039	0.011	2-Methyl octane	NA	NA
3-Ethyltoluene	0.210	0.037	2,3-Dimethyl heptane	NA	NA
P-Ethyltoluene	NA	0.056	Octanoic acid	NA	NA
1,3,5-Trimethylbenzene	NA	<0.005	Octane	NA	NA
1,2,4-Trimethylbenzene	0.250	0.110	Nonane	NA	NA
Naphthalene	0.130	NA	Decane	NA	NA
Acenaphthylene	<0.01	NA	Undecane	NA	NA
Acenaphthene	<0.01	NA	Dodecane	NA	NA
Fluorene	<0.01	NA	Tridecane	NA	NA
Phenanthrene	<0.01	NA	Tetradecane	NA	NA
Anthracene	<0.01	NA	Pentadecane	NA	NA
Fluoranthene	<0.01	NA	Hexadecane	NA	NA
Benzo(a)pyrene	<0.02	NA	Heptadecane	NA	NA
Indeno(1,2,3-cd)pyrene	<0.03	NA	Octadecane	NA	NA
Dibenzo(a,h)anthracene	<0.03	NA	Nonadecane	NA	NA
Benzo(g,h,i)perylene	<0.03	NA	Eicosane	NA	NA
Pyrene	<0.01	NA			

NQ - not quantified

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L)  
NOVEMBER 1986 AND AUGUST 1988 (CONTINUED)

Compound	EA2							
	11/86	01/87	03/87	07/87	09/87	01/88	03/88	08/88
Benzene	0.720	0.710	0.110	0.003	0.012	<0.02	<0.01	0.004
Toluene	2.200	2.900	0.740	0.009	0.510	0.070	0.048	0.003
Ethylbenzene	0.350	0.290	<0.01	<0.002	0.210	0.150	0.140	0.056
m-Xylene	1.900	2.100	2.100	0.033	0.770	0.370	0.380	0.150
o-p Xylenes	2.700	3.000	2.900	0.093	1.000	0.760	0.700	0.340
2-Methylbutane	NQ	NQ	0.046	<0.005	0.089	0.100	0.110	0.032
Pentane	NQ	NQ	<0.03	<0.005	0.054	<0.05	0.067	0.015
Cyclohexane	0.160	0.180	0.240	0.030	<0.03	0.140	0.160	0.058
3-Methylpentane	NQ	NQ	0.088	0.019	0.099	0.060	0.085	0.034
Hexane	NQ	NQ	<0.03	0.012	0.065	<0.05	0.052	0.020
Methylcyclohexane	NQ	NQ	0.270	0.120	0.210	0.130	0.140	0.062
3-Methylhexane	NQ	NQ	0.067	0.035	0.410	<0.05	0.043	0.020
Heptane	NQ	NQ	<0.03	0.019	<0.03	<0.05	<0.01	0.010
Propylbenzene	NQ	<0.05	<0.03	<0.005	0.044	<0.05	<0.033	0.016
3-Ethyltoluene	0.270	0.310	0.320	0.120	0.190	0.130	0.140	0.071
p-Ethyltoluene	NQ	NQ	0.350	0.220	0.190	0.120	0.130	0.068
1,3,5-Trimethylbenzene	NQ	NQ	0.290	0.190	0.120	0.800	0.130	<0.005
1,2,4-Trimethylbenzene	0.380	0.660	0.780	0.130	0.210	0.320	0.270	0.160
Naphthalene	0.170	NQ	0.130	0.039	0.091	0.098	0.062	<0.002
Acenaphthylene	<0.01	NQ	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Acenaphthene	<0.01	NQ	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Fluorene	<0.01	NQ	<0.008	<0.008	<0.002	<0.003	<0.002	<0.002
Phenanthrene	<0.01	NQ	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Anthracene	<0.01	NQ	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Fluoranthene	<0.01	NQ	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Benzo(a)pyrene	<0.02	<0.02	<0.02	<0.004	<0.004	<0.004	<0.004	<0.004
Indeno(1,2,3-cd)pyrene	<0.03	<0.02	<0.02	<0.006	<0.006	<0.006	<0.006	<0.006
Dibenzo(a,h)anthracene	<0.03	<0.02	<0.02	<0.006	<0.006	<0.006	<0.006	<0.006
Benzo(g,h,i)perylene	<0.03	<0.02	<0.02	<0.006	<0.006	<0.006	<0.006	<0.006
Pyrene	<0.01	NQ	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Benzo(a)anthracene	<0.01	NQ	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Crysene	<0.01	NA	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Benzo(b+k)fluoranthene	<0.02	NA	<0.02	<0.02	<0.004	<0.004	<0.004	<0.004
Phenol	0.017	NA	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
2,4-Dimethylphenol	0.019	NA	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
2-Methylphenol	NA	NA	<0.02	<0.02	<0.006	<0.006	<0.006	<0.006

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L.)  
NOVEMBER 1986 AND AUGUST 1988 (CONTINUED)

Compound	EA2							
	11/86	01/87	03/87	07/87	09/87	01/88	03/88	08/88
4-Methylphenol	NQ	NA	0.01	<0.02	<0.006	<0.006	<0.006	<0.006
Benzoic acid	NQ	NA	<0.2	<0.2	<0.05	<0.005	<0.005	<0.05
2-Methylnaphthalene	0.076	NA	0.087	0.120	0.043	<0.002	<0.002	<0.002
1-Methylnaphthalene	0.083	NA	0.094	0.150	0.054	0.063	0.029	<0.002
2,6-Dimethylphenol	NQ	NA	<0.008	<0.008	<0.002	<0.002	<0.002	<0.002
Octanol	NQ	NA	<0.02	<0.02	<0.006	0.057	<0.006	<0.006
2,4-Dimethylbenzoic acid	NQ	NA	0.15	<0.02	<0.05	0.050	<0.05	<0.05
2-Methyl octane	NQ	NA	<0.02	0.550	<0.004	0.053	0.004	<0.004
2,3-Dimethyl heptane	NQ	NA	0.014	0.240	<0.004	0.023	<0.004	<0.004
Octanoic acid	NQ	NA	<0.2	<0.08	<0.05	<0.05	<0.05	<0.05
Octane	NQ	NA	0.015	0.140	<0.01	<0.01	0.030	<0.01
Nonane	NQ	NA	0.017	0.450	<0.01	0.033	<0.01	<0.01
Decane	NQ	NA	0.190	0.700	<0.01	0.095	<0.01	<0.01
Undecane	NQ	NA	0.053	1.200	0.046	0.360	0.012	<0.01
Dodecane	NQ	NA	0.110	1.400	0.083	0.500	0.024	<0.001
Tridecane	NQ	NA	0.110	1.500	0.130	0.610	0.034	<0.1
Tetradecane	NQ	NA	0.120	1.500	<0.01	0.620	0.032	0.014
Pentadecane	NQ	NA	0.080	0.800	0.100	0.340	<0.002	<0.01
Hexadecane	NQ	NA	0.038	0.330	<0.01	0.150	<0.01	<0.01
Heptadecane	NQ	NA	<0.04	0.110	<0.01	0.680	<0.01	<0.01
Octadecane	NQ	NA	<0.04	<0.04	<0.01	0.140	<0.01	<0.01
Nonadecane	NQ	NA	<0.04	<0.04	<0.01	<0.01	<0.01	<0.01
Eicosane	NQ	NA	<0.04	<0.04	<0.01	<0.01	<0.01	<0.01

NQ - not quantified

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L)  
NOVEMBER 1986 AND AUGUST 1988 (CONTINUED)

Compound	11/86	03/87	07/87	09/87	01/88	03/88	08/88
Benzene	3.800	3.600	1.900	1.700	2.400	1.100	1.300
Toluene	2.500	5.900	2.100	2.400	1.400	2.100	<0.002
Ethylbenzene	0.200	0.310	0.230	0.580	0.460	0.630	0.890
m-Xylene	2.200	2.800	1.300	2.400	2.300	2.400	2.900
o-p Xylenes	2.400	3.200	1.800	2.800	2.600	2.700	3.000
2-Methylbutane	0.140	0.470	0.290	0.170	0.490	0.390	0.940
Pentane	0.160	<0.3	0.090	<0.1	0.170	<0.04	0.350
Cyclohexane	NQ	0.270	0.120	<0.1	0.180	0.130	0.390
3-Methylpentane	NQ	<0.3	<0.08	<0.1	<0.1	<0.04	0.120
Hexane	NQ	<0.3	<0.08	<0.1	<0.1	<0.04	0.140
Methylcyclohexane	NQ	<0.3	<0.08	<0.1	0.180	0.120	0.210
3-Methylhexane	NQ	<0.3	<0.08	0.140	<0.1	<0.04	0.530
Heptane	NQ	<0.3	<0.08	<0.1	<0.1	<0.04	0.150
Propylbenzene	<0.05	<0.3	<0.08	<0.1	<0.1	<0.04	0.006
3-Ethyltoluene	<0.05	<0.3	<0.08	<0.1	<0.1	<0.04	0.006
p-Ethyltoluene	NQ	0.390	0.220	0.540	0.390	0.400	0.390
1,3,5-Trimethylbenzene	NQ	<0.3	0.150	0.390	0.270	0.440	0.260
1,2,4-Trimethylbenzene	0.300	0.350	0.380	1.000	0.650	0.650	0.750
Naphthalene	0.170	0.240	0.200	0.410	0.300	0.500	0.300
Acenaphthylene	<0.01	<0.008	<0.008	<0.008	<0.008	0.024	<0.002
Acenaphthene	<0.01	<0.008	<0.008	0.010	0.009	<0.008	<0.002
Fluorene	<0.01	<0.008	<0.008	0.015	0.008	<0.008	<0.002
Phenanthrene	<0.01	<0.008	<0.008	0.019	0.012	<0.008	<0.002
Anthracene	<0.01	<0.008	<0.008	<0.008	<0.008	0.024	<0.002
Fluoranthene	<0.01	<0.008	<0.008	0.013	<0.008	<0.008	<0.002
Benzo(a)pyrene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.004
Indeno(1,2,3-cd)pyrene	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.006
Dibenzo(a,h)anthracene	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.006
Benzo(g,h,i)perylene	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.006
Pyrene	<0.01	<0.008	<0.008	0.011	<0.008	0.024	<0.002
Benzo(a)anthracene	<0.01	<0.008	<0.008	<0.008	<0.008	<0.008	<0.002
Crysene	<0.01	<0.008	<0.008	<0.008	<0.008	<0.008	<0.002
Benzo(b,k)fluoranthene	0.02	<0.02	0.02	<0.02	<0.02	0.016	<0.004
Phenol	0.032	<0.008	0.010	0.012	0.029	<0.008	0.052
2,4-Dimethylphenol	<0.01	<0.008	<0.008	<0.008	0.008	<0.008	0.051
2-Methylphenol	NQ	0.021	0.01	<0.02	0.02	<0.01	<0.006

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L)  
NOVEMBER 1986 AND AUGUST 1988 (CONTINUED)

Compound	EA5						
	11/86	03/87	07/87	09/87	01/88	03/88	08/88
4-Methylphenol	NQ	<0.02	0.100	0.130	<0.02	0.024	<0.006
Benzoic acid	NQ	0.1	<0.2	<0.2	<0.2	<0.2	<0.05
2-Methylnaphthalene	0.070	0.110	0.100	0.240	<0.008	<0.008	0.120
1-Methylnaphthalene	0.085	0.110	0.140	0.270	0.160	0.540	0.012
2,6-Dimethylphenol	NQ	0.023	<0.008	0.084	<0.008	<0.008	0.003
Octanol	NQ	<0.02	<0.02	1.400	0.087	<0.02	<0.006
2,4-Dimethylbenzoic acid	NQ	<0.2	<0.2	<0.2	<0.2	0.320	<0.05
2-Methyl octane	NQ	<0.02	0.550	<0.02	0.120	1.100	0.022
2,3-Dimethyl heptane	NQ	0.072	0.170	0.240	<0.02	1.600	0.011
Octanoic acid	NQ	<0.2	<0.08	<0.2	<0.2	<0.08	<0.05
Octane	NQ	0.076	0.120	0.170	0.080	1.500	0.170
Nonane	NQ	0.150	0.370	0.920	0.180	1.500	0.190
Decane	NQ	0.480	0.770	1.800	0.360	3.100	0.130
Undecane	NQ	0.510	0.980	3.400	0.800	4.200	0.200
Dodecane	NQ	0.580	1.200	3.200	0.820	4.700	0.310
Tridecane	NQ	0.630	1.200	3.500	0.840	3.700	0.240
Tetradecane	NQ	0.520	1.000	2.300	1.000	4.500	0.060
Pentadecane	NQ	0.290	0.600	1.200	0.460	2.500	<0.01
Hexadecane	NQ	0.100	0.210	0.370	0.150	0.050	<0.01
Heptadecane	NQ	0.020	0.060	0.120	0.050	<0.04	<0.01
Octadecane	NQ	<0.04	<0.04	<0.04	<0.04	<0.04	<0.01
Nonadecane	NQ	<0.04	<0.04	<0.04	<0.04	<0.04	<0.01
Eicosane	NQ	<0.04	<0.04	<0.04	<0.04	<0.04	<0.01

NQ - not quantified

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L)  
NOVEMBER 1986 AND AUGUST 1988 (CONTINUED)

Compound	EA8					
	11/86	03/87	07/87	09/87	01/88	03/88 08/88
Benzene	0.910	<0.04	0.050	<0.03	<0.03	0.023
Toluene	1.600	2.700	1.300	0.620	0.820	0.007
Ethylbenzene	0.100	0.250	0.190	0.370	0.380	0.041
m-Xylene	1.500	2.800	1.200	1.600	1.900	0.120
o-p Xylenes	1.900	3.500	1.700	2.600	2.700	0.120
2-Methylbutane	0.089	<0.1	<0.08	<0.08	0.110	0.005
Pentane	NQ	<0.1	<0.08	<0.075	<0.08	<0.005
Cyclohexane	0.075	<0.1	<0.08	<0.075	0.110	0.042
3-Methylpentane	NQ	<0.1	<0.08	<0.075	<0.08	0.025
Hexane	NQ	<0.1	<0.08	<0.075	<0.08	0.023
Methylcyclohexane	NQ	0.110	0.110	0.150	0.120	0.110
3-Methylhexane	NQ	<0.1	0.080	<0.075	<0.08	0.028
Heptane	NQ	<0.1	0.080	<0.075	<0.08	0.023
Propylbenzene	<0.02	<0.1	0.080	<0.075	<0.08	0.027
3-Ethyltoluene	0.250	0.400	0.160	0.330	0.250	0.280
p-Ethyltoluene	NQ	0.440	0.290	0.460	0.350	0.320
1,3,5-Trimethylbenzene	NQ	0.310	0.170	0.320	0.280	0.300
1,2,4-Trimethylbenzene	0.700	0.890	0.400	0.730	0.650	0.630
Naphthalene	NQ	0.240	0.240	0.240	0.410	0.035
Acenaphthylene	NQ	<0.008	<0.008	<0.008	0.009	<0.002
Acenaphthene	NQ	<0.008	<0.008	<0.008	0.012	0.002
Fluorene	NQ	<0.008	<0.008	<0.008	0.011	<0.002
Phenanthrene	0.140	<0.008	<0.008	<0.008	<0.008	<0.002
Anthracene	<0.01	<0.008	<0.008	<0.008	<0.008	<0.002
Fluoranthene	<0.01	<0.008	<0.008	<0.008	<0.008	<0.002
Pyrene	<0.01	<0.008	<0.008	<0.008	<0.008	<0.002
Benzo(a)anthracene	<0.01	<0.008	<0.008	<0.008	<0.008	<0.002
Crysene	0.01	<0.008	<0.008	<0.008	<0.008	<0.002
Benzo(b+k)fluoranthene	<0.01	<0.02	<0.02	<0.02	<0.02	<0.004
Benzo(a)pyrene	<0.01	<0.02	<0.02	<0.02	<0.02	<0.004
Indeno(1,2,3-cd)pyrene	<0.01	<0.02	<0.02	<0.02	<0.02	<0.006
Dibenzo(a,h)anthracene	<0.01	<0.02	<0.02	<0.02	<0.02	<0.006
Benzo(g,h,i)perylene	<0.01	<0.02	<0.02	<0.02	<0.02	<0.006
Phenol	<0.01	0.008	0.017	0.008	<0.008	0.002
2,4-Dimethylphenol	<0.01	<0.008	<0.008	<0.008	<0.008	0.002
2-Methylphenol	11	0.02	<0.02	0.01	<0.02	<0.002

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L)  
NOVEMBER 1986 AND AUGUST 1988 (CONTINUED)

Compound	EA8						
	11/86	03/87	07/87	09/87	01/88	03/88	08/88
4-Methylphenol	NQ	<0.02	0.070	<0.02	<0.02	<0.02	<0.006
Benzoic acid	NQ	<0.2	<0.2	<0.2	<0.2	<0.2	<0.05
2-Methylnaphthalene	0.081	0.150	0.130	0.089	<0.008	<0.008	0.150
1-Methylnaphthalene	0.084	0.170	0.150	0.120	0.280	0.300	0.017
2,6-Dimethylphenol	NQ	<0.008	<0.008	<0.008	<0.008	<0.008	<0.002
Octanol	NQ	<0.02	0.360	0.130	0.470	1.400	<0.006
2,4-Dimethylbenzoic acid	NQ	<0.2	<0.2	<0.2	<0.2	0.280	<0.05
2-Methyl octane	NQ	0.210	0.310	0.160	0.470	1.200	0.015
2,3-Dimethyl heptane	NQ	0.110	0.200	0.066	0.260	1.500	0.06
Octanoic acid	NQ	<0.2	<0.08	<0.2	<0.2	<0.2	<0.05
Octane	NQ	0.037	0.060	<0.04	0.130	0.180	0.019
Nonane	NQ	0.110	0.140	<0.04	0.460	0.630	0.036
Decane	NQ	0.370	0.330	0.120	0.730	1.600	0.059
Undecane	NQ	0.520	0.750	0.340	1.600	3.200	0.140
Dodecane	NQ	0.780	1.400	0.590	1.900	3.600	0.290
Tridecane	NQ	1.100	1.500	0.880	2.300	3.700	0.570
Tetradecane	NQ	1.100	1.400	8.300	2.800	5.200	0.890
Pentadecane	NQ	0.710	0.960	0.500	1.800	3.000	<0.01
Hexadecane	NQ	0.310	0.390	0.150	0.640	1.200	<0.01
Heptadecane	NQ	0.093	0.080	<0.04	0.180	<0.04	<0.01
Octadecane	NQ	0.018	<0.04	<0.04	0.040	<0.04	<0.01
Nonadecane	NQ	<0.04	<0.04	<0.04	<0.04	<0.04	<0.01
Eicosane	NQ	<0.04	<0.04	<0.04	<0.04	<0.04	<0.01

NQ - not quantified

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L.)  
NOVEMBER 1986 AND AUGUST 1988 (CONTINUED)

Compound	EA19			
	03/87	07/87	09/87	01/88 03/88 08/88
Benzene	0.380	0.080	<0.016	<0.006 <0.004 <0.002
Toluene	4.300	1.600	0.720	<0.006 <0.004 <0.003
Ethylbenzene	0.180	0.390	0.430	0.065 0.010 0.007
m-Xylene	2.100	1.900	1.700	0.230 0.019 0.007
o-p Xylenes	2.700	2.200	2.000	0.550 0.084 0.022
2-Methylbutane	0.099	6.190	0.150	<0.015 0.017 0.007
Pentane	0.082	<0.08	0.099	<0.015 <0.004 0.005
Cyclohexane	0.260	0.200	<0.04	0.022 0.080 0.034
3-Methylpentane	0.260	0.110	0.160	<0.015 0.092 0.058
Hexane	NQ	0.110	0.140	<0.02 0.063 0.047
Methylcyclohexane	NQ	0.200	0.300	0.022 0.180 0.150
3-Methylhexane	0.099	<0.08	0.068	<0.015 0.044 0.038
Heptane	NQ	<0.08	0.051	<0.015 0.030 0.023
Propylbenzene	<0.05	<0.08	0.095	0.029 0.028 0.020
3-Ethyltoluene	0.260	0.210	0.420	0.150 0.130 0.078
p-Ethyltoluene	NQ	0.230	0.440	0.140 0.110 0.069
1,3,5-Trimethylbenzene	NQ	0.130	0.260	0.070 0.110 0.057
1,2,4-Trimethylbenzene	0.340	0.450	0.860	0.350 0.220 0.180
Naphthalene	<0.008	0.190	0.160	0.019 0.012 0.012
Acenaphthylene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Acenaphthene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Fluorene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Phenanthrene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Anthracene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Fluoranthene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Pyrene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Benzo(a)anthracene	<0.008	<0.008	<0.002	<0.002 <0.002 <0.002
Crysene	<0.02	<0.02	<0.004	<0.004 <0.004 <0.004
Benzo(b+k)fluoranthene	<0.02	<0.02	<0.004	<0.004 <0.004 <0.004
Benzo(a)pyrene	<0.02	<0.02	<0.006	<0.006 <0.006 <0.006
Indeno(1,2,3-cd)pyrene	<0.02	<0.02	<0.006	<0.006 <0.006 <0.006
Dibenzo(a,h)anthracene	<0.02	<0.02	<0.006	<0.006 <0.006 <0.006
Benzo(g,h,i)perylene	<0.006	<0.02	<0.002	<0.002 <0.002 <0.002
Phenol	<0.008	0.011	0.005	0.002 0.002 0.002
2,4-Dimethylphenol	<0.008	0.008	0.005	0.002 0.002 0.002
2-Methylphenol	0.01	<0.01	0.006	0.006 0.006 0.006

TABLE 17. JP-4 COMPONENTS IN GROUNDWATER AT THE EGLIN POL DEMONSTRATION SITE mg/L)  
NOVEMBER 1986 AND AUGUST 1988 (CONCLUDED)

Compound	EA19				
	03/87	07/87	09/87	01/88	08/88
4-Methylphenol	0.02	0.080	0.008	<0.006	<0.006
Benzoic acid	<0.2	<0.2	<0.05	<0.05	<0.05
2-Methylnaphthalene	<0.008	0.054	0.074	<0.002	0.048
1-Methylnaphthalene	<0.008	0.067	0.100	0.035	0.003
2,6-Dimethylphenol	<0.008	0.030	<0.002	<0.002	<0.002
Octanol	<0.02	<0.02	<0.006	<0.006	<0.006
2,4-Dimethylbenzoic acid	<0.2	<0.2	<0.05	<0.05	<0.05
2-Methyl octane	<0.02	<0.02	<0.004	0.017	<0.004
2,3-Dimethyl heptane	<0.02	0.040	<0.004	<0.004	<0.004
Octanoic acid	0.07	0.150	<0.05	<0.05	<0.05
Octane	<0.04	0.080	<0.01	<0.01	<0.01
Nonane	<0.04	<0.04	<0.01	<0.01	<0.01
Decane	<0.04	0.110	<0.01	<0.01	<0.01
Undecane	<0.04	<0.04	<0.01	<0.01	<0.01
Dodecane	<0.04	<0.04	<0.01	<0.01	<0.01
Tridecane	<0.04	<0.04	<0.01	<0.01	<0.01
Tetradecane	<0.04	<0.04	<0.01	<0.01	<0.01
Pentadecane	<0.04	<0.04	<0.01	<0.01	<0.01
Hexadecane	<0.04	<0.04	<0.01	<0.01	<0.01
Heptadecane	<0.04	<0.04	<0.01	<0.01	<0.01
Octadecane	<0.04	<0.04	<0.01	<0.01	<0.01
Nonadecane	<0.04	<0.04	<0.01	<0.01	<0.01
Eicosane	<0.04	<0.04	<0.01	<0.01	<0.01

NQ - not quantified

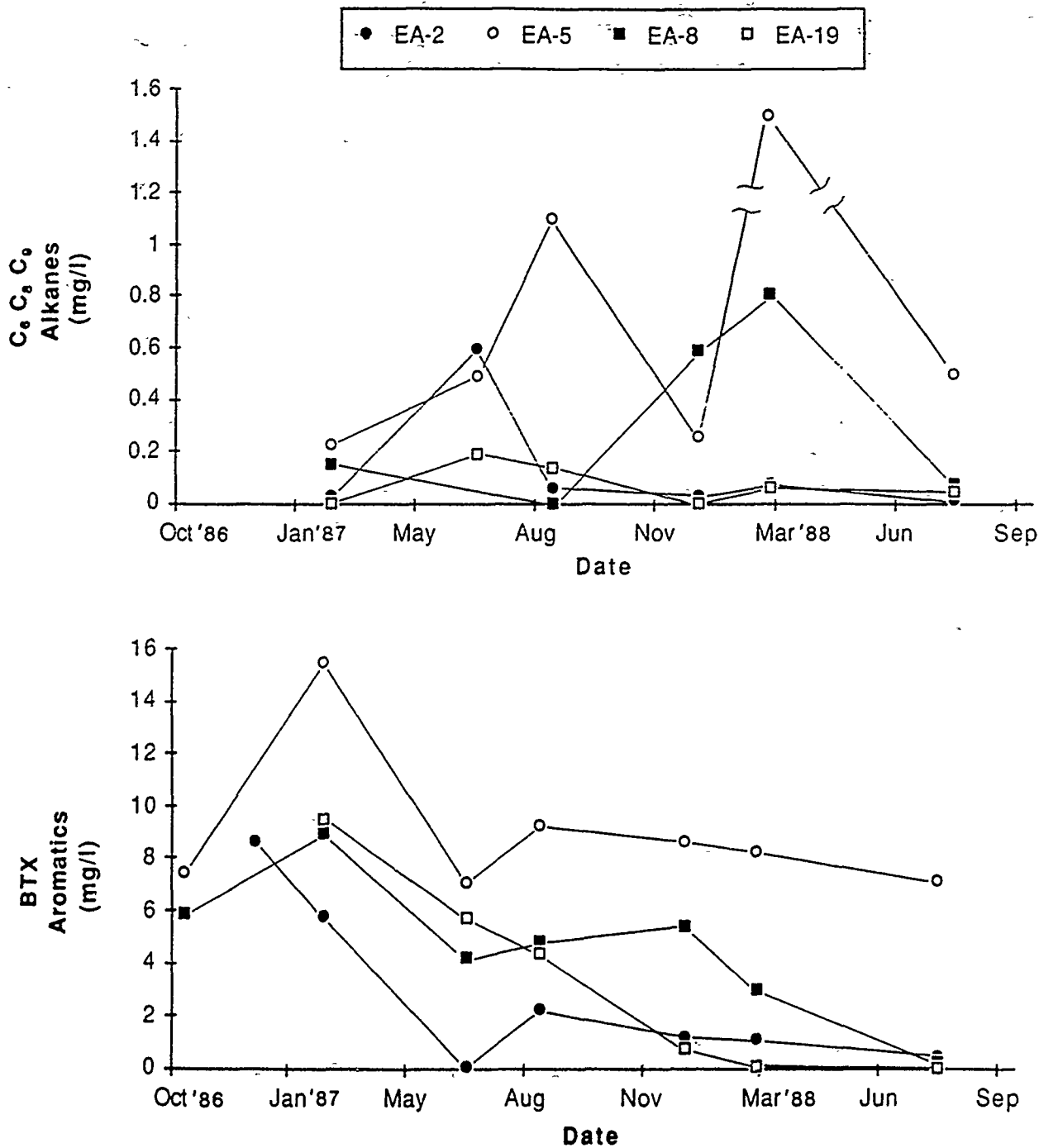


Figure 27. Behavior of Selected JP-4 Constituents in Groundwater from Selected Wells at the Eglin POL Demonstration Site.

TABLE 18. TOTAL PETROLEUM HYDROCARBON (TPH) CONCENTRATIONS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg)

Location	Depth (ft)	11/86	01/87	03/87	07/87	09/87	01/88	03/88	08/88
B, C <sup>a</sup>		390	--	--	--	--	--	--	1,500
D, C <sup>a</sup>		620	--	--	--	--	--	--	--
EA1	0.5	240	--	--	--	--	--	--	--
EA1	1	220	--	--	50	--	--	--	27
EA1	2	230	--	--	40	--	--	--	22
EA1	3	280	--	--	60	--	--	--	40
EA1	4	220	--	--	--	--	--	--	44
EA1	5	--	--	--	--	--	--	--	23
EA2	0.5	--	--	--	560	--	--	--	--
EA2	1	2,100	--	80	--	20	<10	<10	1,700
EA2	2	2,200	--	2,000	530	780	<10	690	1,900
EA2	3	3,300	--	1,800	90	120	<10	<10	33
EA2	4	240	--	290	--	20	<10	<10	15
EA2	5	220	--	--	--	<10	--	<10	33
EA3, C <sup>a</sup>	0.5	900	--	--	--	--	--	--	910
EA3	1	--	--	--	80	--	--	--	--
EA3	2	--	--	--	1,100	800	1,300	840	1,300
EA3	3	--	--	--	--	--	1,800	9,600	2,300
EA3	4	--	--	--	310	160	1,700	3,100	540
EA3		--	--	--	--	--	1,000	--	230
EA4, C <sup>a</sup>		750	--	--	--	--	--	--	530
EA4	1	--	--	--	--	--	<10	--	74
EA4	2	--	--	--	120	--	--	--	--
EA4	3	--	--	--	--	180	--	--	1,300
EA4	4	--	--	--	770	--	2,100	--	1,100
EA4	5	--	--	--	--	160	--	--	1,100
EA4	6	--	--	--	1,000	--	2,100	--	480
EA4		--	--	--	--	--	490	--	710
EA5	1	--	420	130	90	20	--	40	34
EA5	2	--	110	230	120	90	1,400	660	75
EA5	3	2,100	130	170	90	90	2,600	11,000	730
EA5	4	650	--	1,000	240	1,100	14,000	1,900	600
EA5	5	3,900	--	2,200	4,700	540	4,500	3,600	560
EA5	6	220	--	820	--	400	<10	<10	350
EA5	7	200	--	--	--	20	--	10	74

TABLE 18. TOTAL PETROLEUM HYDROCARBON (TPH) CONCENTRATIONS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg) (CONCLUDED)

Location	Depth (ft)	11/86	01/87	03/87	07/87	08/87	01/88	03/88	08/88
EA6,C <sup>a</sup>									
EA6	1	210	--	--	--	--	--	--	58
EA6	3	--	--	--	120	--	--	--	70
EA6	5	--	--	--	90	20	520	<10	77
EA6	--	--	--	--	100	<20	480	<10	71
EA7,C <sup>a</sup>									
EA7	1	810	--	--	--	--	--	--	830
EA7	2	--	--	--	80	--	--	--	38
EA7	3	--	--	--	180	--	--	--	52
EA7	4	--	--	--	--	--	--	--	660
EA8	1	--	--	--	540	--	--	--	360
EA8	2	--	10,000	90	90	<20	80	<10	14
EA8	3	--	130	80	110	90	3,200	<10	1,800
EA8	4	2,800	100	690	--	870	2,000	1,100	3,600
EA8	5	2,500	--	220	1,200	1,200	17,000	7,300	1,300
EA8	6	740	--	1,000	850	<20	460	3,00	2,100
EA8	7	230	--	--	--	<20	<10	<10	1,700
EA8	--	220	--	--	--	--	--	<10	24
EA18	1	--	--	80	40	<20	<10	<10	59
EA18	2	--	--	1,800	3,000	--	1,900	<10	110
EA18	3	--	--	520	940	190	1,300	890	1,500
EA18	4	--	--	--	850	--	1,100	--	420
EA18	5	--	--	--	--	20	930	--	540
EA19	1	--	--	--	50	<20	<10	70	42
EA19	2	--	--	--	1,850	1,600	4,300	1,300	2,200
EA19	3	--	--	--	390	130	2,200	490	390
EA19	4	--	--	--	40	<20	70	<10	180
EA19	5	--	--	--	--	40	<10	<10	51
EA25	4	--	--	--	--	--	2,200	--	--
EA25	5	--	--	--	--	--	3,900	--	--
EA25	6	--	--	--	--	--	720	--	--
EA29	3	--	--	--	--	--	--	910	--
EA29	4	--	--	--	--	--	--	1,800	--
EA29	5	--	--	--	--	--	--	3,100	--
EA31	3	--	--	--	--	--	--	3,100	--

<sup>a</sup> composite sample of selected depths.

<sup>b</sup> -- = not analyzed.

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg)

Compound	EA2						
	11/86	03/87	07/87	09/87	01/88	03/88	08/88
Benzene	2.2	<0.1	<1	<0.2	<0.01	<0.01	<2
Toluene	37	2.8	<1	<0.2	<0.01	<0.01	4
Ethylbenzene	16	1.3	<1	<0.2	<0.01	<0.01	4.4
m-Xylene	60	9.6	3	6.8	<0.01	<0.01	18
o+p Xylenes	69	17	4	18	<0.01	0.075	28
2-Methylbutane	NQ	NQ	<3	<0.5	<0.025	0.011	<5
Pentane	NQ	NQ	<3	<0.5	<0.025	<0.01	<5
Cyclohexane	4	1.3	<3	<0.5	<0.025	0.2	4.3
3-Methylpentane	2.7	0.87	<3	<0.5	<0.025	0.48	5.6
Hexane	NQ	-	<3	<0.5	<0.025	0.46	9.5
Methylcyclohexane	NQ	5.8	5	1.9	<0.025	3.2	18
3-Methylhexane	4.9	3.9	6	<0.5	<0.025	2.9	17
Heptane	NQ	1.5	3	<0.5	<0.025	2.7	14
Propylbenzene	2.9	0.33	<3	0.66	<0.025	0.11	2.6
3-Ethyltoluene	13	4.4	3	5.4	<0.025	0.094	13
p-Ethyltoluene	NQ	6.3	4	5.8	<0.025	1.8	12
1,3,5-Trimethylbenzene	NQ	4.6	6	4.7	<0.025	<0.01	<5
1,2,4-Trimethylbenzene	19	8	6	10	<0.025	<0.01	<5
Naphthalene	3.9	16	7.7	53	<0.1	<0.2	7.2
Acenaphthylene	<0.5	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
Acenaphthene	<0.1	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
Fluorene	0.59	0.94	1.6	0.45	<0.1	<0.2	<0.4
Phenanthrene	<0.5	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
Anthracene	<0.5	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
Fluoranthene	<0.5	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
Pyrene	<0.5	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
Benzo(a)anthracene	<0.5	<0.5	<0.4	<0.4	<0.2	<0.4	<0.4
Crysene	<0.5	<0.5	<0.4	<0.4	<0.2	<0.4	<0.4
Benzo(b+k)fluoranthene	<1	<1	<0.8	<0.7	<0.2	<0.4	<0.4
Benzo(a)pyrene	<1	<1	<0.8	<0.7	<0.3	<0.6	<0.8
Indeno(1,2,3-cd)pyrene	<1	<1	<1	<1	<0.5	<1	<1
Dibenzo(a,h)anthracene	<1	<1	<1	<1	<0.5	<1	<1
Benzo(g,h,i)perylene	<1	<1	<1	<1	<0.5	<1	<1
Phenol	<0.5	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
2,4-Dimethylphenol	<0.5	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
2-Methylphenol	NQ	<1	<1	<1	<0.3	<0.6	<1
4-Methylphenol	NQ	<1	<1	<1	<0.3	0.6	<1
Benzoic acid	NQ	<10	<10	<10	<2.5	<5	<10
2-Methylnaphthalene	12	23	12	8	<0.1	1.5	20
1-Methylnaphthalene	8.3	23	17	10	<0.1	1.9	1.4
2,6-Dimethylphenol	NQ	<0.5	<0.4	<0.4	<0.1	<0.2	<0.4
Octanol	NQ	<1	<1	31	<0.3	<0.6	<1
2,4-Dimethylbenzoic acid	NQ	<10	<10	<9	<2.5	<5	<10
2-Methyl octane	3.3	<1	150	70	<0.2	23	<0.8
2,3-Dimethyl heptane	NQ	<1	150	35	<0.2	30	<0.8

NQ - not quantified

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg)  
(CONTINUED)

Compound	EA2						
	11/86	03/87	07/87	09/87	01/88	03/88	08/88
Octanoic acid	NQ	<10	<4	<9	<2.5	<5	<10
Octane	NQ	92	62	31	<0.5	1.9	63
Nonane	NQ	160	90	68	<0.5	31	110
Decane	NQ	140	88	70	<0.5	28	110
Undecane	NQ	190	150	92	<0.5	35	150
Dodecane	NQ	160	170	89	<0.5	37	140
Tridecane	NQ	170	200	91	<0.5	31	130
Tetradecane	NQ	140	190	80	<0.5	25	110
Pentadecane	NQ	88	110	47	<0.5	17	60
Hexadecane	NQ	35	60	18	<0.5	6.4	19
Heptadecane	NQ	8.4	14	7.3	<0.5	1.8	4.7
Octadecane	NQ	2.4	4	<2	<0.5	<1	<2
Nonadecane	NQ	1	<2	<2	<0.5	<1	<2
Eicosane	NQ	<2	<2	<2	<0.5	<1	<2

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN PCL DEMONSTRATION SITE (mg/kg)  
(CONTINUED)

Compound	EA5						
	11/86	03/87	07/87	09/87	01/88	03/88	08/88
Benzene	<0.8	<0.04	<0.01	<0.5	<0.6	<1	<1
Toluene	2.6	0.43	<0.01	0.67	5.4	<1	1.2
Ethylbenzene	12	1.4	<0.01	0.99	14	44	5.2
m-Xylene	44	10	<0.01	17	54	130	24
o+p Xylenes	33	9.4	<0.01	16	60	130	16
2-Methylbutane	NQ	<0.1	<0.03	<1	<1.5	<1	<2.5
Pentane	NQ	<0.1	<0.03	<1	<1.5	<1	<2.5
Cyclohexane	0.9	0.42	<0.03	<1	1.5	15	1.5
3-Methylpentane	NQ	0.32	<0.03	<1	<1.5	26	2.5
Hexane	NQ	0.55	<0.03	<1	1.7	38	4.9
Methylcyclohexane	NQ	1.9	<0.03	6.2	9.1	<1	10
3-Methylhexane	1.1	1.4	<0.03	5.3	6.4	160	7.2
Heptane	NQ	1.4	<0.03	7.3	10	230	14
Propylbenzene	1.8	0.7	<0.03	<1	4	<1	4.4
3-Ethyltoluene	8.9	4.2	<0.03	7	15	68	17
p-Ethyltoluene	NQ	4.1	<0.03	6.5	14	58	13
1,3,5-Trimethylbenzene	NQ	3	<0.03	1.8	7.2	<1	2.5
1,2,4-Trimethylbenzene	12	12	<0.03	19	33	140	43
Naphthalene	6.7	11	<0.1	11	55	3.3	5
Acenaphthylene	<0.5	<0.5	<0.1	<0.4	<1	<0.09	<0.4
Acenaphthene	<0.5	1.3	<0.1	1	<1	<0.09	<0.4
Fluorene	0.59	1.5	<0.1	1.1	<1	<0.09	<0.4
Phenanthrene	<0.5	4.6	<0.1	3	<1	<0.09	<0.4
Anthracene	<0.5	1.2	<0.1	0.86	<1	<0.09	<0.4
Fluoranthene	<0.5	4.4	<0.1	2.5	1.5	<0.09	<0.4
Pyrene	<0.5	3.4	<0.1	3.4	1.3	<0.09	<0.4
Benzo(a)anthracene	<0.5	1.5	<0.1	0.91	<2	<0.18	<0.4
Crysene	<0.5	1.4	<0.1	0.95	<2	<0.18	<0.4
Benzo(b+k)fluoranthene	<1	1.7	<0.2	1.9	<2	<0.18	<0.4
Benzo(a)pyrene	<1	<0.9	<0.2	<0.8	<3	<0.27	<0.8
Indeno(1,2,3-cd)pyrene	<1	<1	<0.3	<1	<5	<0.45	<1
Dibenzo(a,h)anthracene	<1	<1	<0.3	<1	<5	<0.45	<1
Benzo(g,h,i)perylene	<1	<1	<0.3	<1	<5	<0.45	<1
Phenol	<0.5	<0.5	<0.1	<0.4	<1	<0.09	<0.4
2,4-Dimethylphenol	<0.5	<0.5	<0.1	<0.4	<1	<0.09	<0.4
2-Methylphenol	NQ	<1	<0.3	<1	<3	<0.27	<1
4-Methylphenol	NQ	<1	<0.3	<1	<3	<0.47	<1
Benzoic acid	NQ	<10	<3	<10	<25	<2.25	<10
2-Methylnaphthalene	16	17	<0.1	12	100	<0.09	11
1-Methylnaphthalene	11	15	<0.1	14	33	2.3	0.79
2,6-Dimethylphenol	NQ	<0.5	<0.1	<0.4	<1	<0.09	<0.4
Octanol	NQ	<1	1.3	39	<3	25	<1
2,4-Dimethylbenzoic acid	NQ	<10	<3	<10	<25	<2.25	<10
2-Methyl octane	3.3	87	<0.2	71	230	28	<0.8
2,3-Dimethyl heptane	NQ	<0.9	<0.2	26	110	9.3	<0.8

NQ - not quantified

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg)  
(CONTINUED.)

Compound	EA5						
	11/86	03/87	07/87	09/87	01/88	03/88	08/88
Octanoic acid	NQ	<10	<1	<10	<25	<2.25	<10
Octane	NQ	47	<0.5	32	240	22	21
Nonane	NQ	100	<0.5	86	240	31	61
Decane	NQ	94	<0.5	87	290	31	65
Undecane	NQ	130	<0.5	120	360	36	95
Dodecane	NQ	120	<0.5	100	440	31	79
Tridecane	NQ	120	<0.5	98	340	27	72
Tetradecane	NQ	95	<0.5	75	220	36	54
Pentadecane	NQ	58	<0.5	37	120	17	23
Hexadecane	NQ	25	<0.5	12	53	<0.45	6.1
Heptadecane	NQ	5.6	<0.5	3.2	17	<0.45	2.1
Octadecane	NQ	2.2	<0.5	<2	7.1	<0.45	<2
Nonadecane	NQ	1.5	<0.5	<2	5.2	<0.45	<2
Eiccosane	NQ	<2	<0.5	<2	<5	<0.45	<2

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN FOL DEMONSTRATION SITE (mg/kg)  
(CONTINUED)

Compound	EA8 11/86	EA8 03/87	EA8 <sup>a</sup> 07/87	EA8 <sup>a</sup> 07/87	EA8 09/87	EA8 01/88	EA8 03/88	EA8 08/88
Benzene	<0.5	<0.2	<0.2	-	<0.2	<0.2	<0.5	<1
Toluene	14	<0.2	<0.2	-	<0.2	0.8	<0.5	<1
Ethylbenzene	9.9	<0.2	<0.2	-	<0.2	1.4	<0.5	<1
m-Xylene	42	24	0.2	-	12	20	22	<2.5
o+p Xylenes	51	27	0.3	-	16	27	29	<2.6
2-Methylbutane	NQ	<0.5	<0.4	-	<0.5	<0.5	<0.5	<2.5
Pentane	NQ	<0.5	<0.1	-	<0.5	<0.5	<0.5	<2.5
Cyclohexane	0.85	0.57	<0.4	-	<0.5	0.8	3.7	<2.5
3-Methylpentane	NQ	<0.5	<0.4	-	<0.5	<0.5	4.6	1
Hexane	NQ	<0.5	<0.4	-	<0.5	<0.5	<0.5	2.6
Methylcyclohexane	NQ	6.8	1.1	-	3.8	4.2	<0.5	17
3-Methylhexane	NQ	4.9	0.6	-	2.6	2.3	54	11
Heptane	NQ	2.2	<0.4	-	1.7	1.5	60	12
Propylbenzene	1.8	<0.5	<0.4	-	0.72	0.9	5.8	<2.5
3-Ethyltoluene	9.2	15	1.4	-	14	8.7	59	<12
p-Ethyltoluene	NQ	15	1.7	-	15	9.1	64	17
1,3,5-Trimethylbenzene	NQ	14	4.1	-	14	6.9	48	<2.5
1,2,4-Trimethylbenzene	12	53	2	-	42	24	140	23
Naphthalene	7.6	7.3	<0.4	<0.4	6.6	57	17	<4
Acenaphthylene	<0.5	<0.5	<0.4	<0.4	<0.4	<1	<0.4	<0.4
Acenaphthene	<0.5	<0.5	<0.4	<0.4	<0.4	<1	<0.4	<0.4
Fluorene	0.71	<0.5	<0.4	<0.4	0.56	<1	2.3	<0.4
Phenanthrene	<0.5	<0.5	<0.4	<0.4	<0.4	1.8	1.8	<0.4
Anthracene	<0.5	<0.5	<0.4	<0.4	<0.4	<1	<0.4	<0.4
Fluoranthene	<0.5	<0.5	<0.4	<0.4	<0.4	<1	2	<0.4
Pyrene	<0.5	<0.5	<0.4	<0.4	<0.4	1.3	0.9	<0.4
Benzo(a)anthracene	<0.5	<0.5	<0.4	<0.4	<0.4	<2	<0.8	<0.4
Crysene	<0.5	<0.5	<0.4	<0.4	<0.4	<2	<0.8	<0.4
Benzo(b+k)fluoranthene	<1	<1	<0.8	<0.8	<0.8	<2	<0.8	<0.4
Benzo(a)pyrene	<1	<1	<0.8	<0.8	<0.8	<3	<1.2	<0.8
Indeno(1,2,3-cd)pyrene	<1	<1	<1	<1	<1	<5	<2	<1
Dibenzo(a,h)anthracene	<1	<1	<1	<1	<1	<5	<2	<1
Benzo(g,h,i)perylene	<1	<1	<1	<1	<1	<5	<2	<1
Phenol	<0.5	<0.5	<0.4	<0.4	<0.4	<1	<0.4	<0.4
2,4-Dimethylphenol	<0.5	<0.5	<0.4	<0.4	<0.4	<1	<0.4	<0.4
2-Methylphenol	NQ	<1	<1	<1	<1	<3	<1.2	<1
4-Methylphenol	NQ	<1	<1	<1	<1	<3	<1.2	<1
Benzoic acid	NW	<10	<10	<10	<10	<25	<10	<10
2-Methylnaphthalene	18	14	<0.4	<0.4	13	150	<0.4	12
1-Methylnaphthalene	13	13	<0.4	<0.4	16	410	<0.4	1.1
2,6-Dimethylphenol	NQ	<0.5	<0.4	<0.4	<0.4	<1	<0.4	<0.4
Octanol	NQ	<1	<1	<1	450	<3	<1.2	<1
2,4-Dimethylbenzoic acid	NQ	<10	<10	<10	<10	<25	<10	<10
2-Methyl octane	NQ	74	21	15	55	260	<0.8	<0.8
2,3-Dimethyl heptane	NQ	35	11	8	40	130	480	<0.8

<sup>a</sup>EA8 was sampled and analyzed in duplicate in July.  
NQ - not quantified

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg)  
(CONTINUED)

Compound	EA8 11/86	EA8 03/87	EA8 07/87	EA8D 07/87	EA8 09/87	EA8 01/88	EA8 03/88	EA8 08/88
Octanoic acid	NQ	<10	<4	<4	<10	<25	<10	<10
Octane	NQ	18	3	<2	22	170	170	<2
Nonane	NQ	48	9	7	57	240	260	70
Decane	NQ	61	11	11	61	290	210	92
Undecane	NQ	82	21	21	86	480	330	140
Dodecane	NQ	87	25	29	85	620	280	150
Tridecane	NQ	95	39	44	98	500	190	160
Tetradecane	NQ	78	54	55	100	260	200	150
Pentadecane	NQ	48	41	40	55	150	120	79
Hexadecane	NQ	18	18	18	30	79	77	25
Heptadecane	NQ	5.6	4	4	5.8	18	16	5.9
Octadecane	NQ	<2	<2	<2	<2	<5	4.1	2
Nonadecane	NQ	<2	<2	<2	<2	<5	<2	<2
Eiccosane	NQ	<2	<2	<2	<2	<5	<2	<2

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg)  
(CONTINUED)

Compound	EA19					
	03/87	07/87	09/87	01/88	03/88	08/88
Benzene	0.5	<2	<2	<0.4	<0.5	<1
Toluene	24	6.1	2.3	0.6	<0.5	<1.1
Ethylbenzene	8	7.6	2.1	2.3	6.1	<1
m-Xylene	29	27	7.5	13	71	3
o+p Xylenes	32	41	8.5	17	88	4.2
2-Methylbutane	NQ	<5	<0.5	<1	7.2	<2.5
Pentane	NQ	<5	<0.5	<1	2.1	<2.5
Cyclohexane	1.6	<5	<0.5	<1	19	0.74
3-Methylpentane	1.2	<5	0.98	<1	28	1
Hexane	NQ	<5	1.2	<1	39	2.7
Methylcyclohexane	NQ	6.8	2.2	3.5	<0.5	7.6
3-Methylhexane	1.6	<5	1.4	1.7	120	4.6
Heptane	NQ	<5	1.4	1.4	140	5.5
Propylbenzene	1.2	<5	0.85	1.1	7.2	1.3
3-Ethyltoluene	5	12	3	5.2	50	7.4
p-Ethyltoluene	NQ	14	2.5	4.8	45	7.2
1,3,5-Trimethylbenzene	NQ	16	2.1	3.3	29	<2.5
1,2,4-Trimethylbenzene	12	28	7.5	11	100	11
Naphthalene	4.5	2.8	8.4	10	11	<4
Acenaphthylene	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Acenaphthene	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Fluorene	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Phenanthrene	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Anthracene	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Fluoranthene	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Pyrene	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Benzo(a)anthracene	NQ	<0.4	<0.4	<0.8	<0.8	<0.4
Crysene	<0.5	<0.4	<0.4	<0.8	<0.8	<0.4
Benzo(b+k)fluoranthene	<1	<0.8	<0.8	<0.8	<0.8	<0.4
Benzo(a)pyrene	<1	<0.8	<0.8	<1.2	<1.2	<0.8
Indeno(1,2,3-cd)pyrene	<1	<1	<1	<2	<2	<1
Dibenzo(a,h)anthracene	<1	<1	<1	<2	<2	<1
Benzo(g,h,i)perylene	<1	<1	<1	<2	<2	<1
Phenol	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
2,4-Dimethylphenol	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
2-Methylphenol	<1	<1	<1	<1.2	<1.2	<1
4-Methylphenol	<1	<1	<1	<1.2	<1.2	<1
Benzoic acid	<10	<10	<10	<10	<10	<10
2-Methylnaphthalene	6.6	4.2	8.9	22	8.4	7.1
1-Methylnaphthalene	6.6	5.6	9.6	9.9	12	0.52
2,6-Dimethylphenol	<0.5	<0.4	<0.4	<0.4	<0.4	<0.4
Octanol	<1	<1	270	<1.2	<1.2	<1
2,4-Dimethylbenzoic acid	<10	<10	<10	<10	<10	<10
2-Methyl octane	<1	41	20	50	33	5.5
2,3-Dimethyl heptane	8.1	19	15	15	87	<0.8

NQ - not quantified

TABLE 19. JP-4 COMPONENTS IN SOIL AT THE EGLIN POL DEMONSTRATION SITE (mg/kg)  
(CONCLUDED)

Compound	EA19					
	03/87	07/87	09/87	01/88	03/88	08/88
Octanoic acid	<10	<4	<10	<10	<10	<10
Octane	16	13	19	30	84	<2
Nonane	25	42	47	67	97	51
Decane	31	54	53	80	82	50
Undecane	48	72	69	95	94	62
Dodecane	53	76	65	110	90	68
Tridecane	49	78	69	87	69	74
Tetradecane	41	66	55	58	53	64
Pentadecane	22	39	33	34	37	32
Hexadecane	72	15	15	11	14	9.5
Heptadecane	<2	3	<2	2.7	3.8	2.5
Octadecane	<2	<2	<2	<2	<2	<2
Nonadecane	<2	<2	<2	<2	<2	<2
Eiccosane	<2	<2	<2	<2	<2	<2

cause of this lack of soil flushing is not clear. It is possible that the infiltration water followed preferential pathways, avoiding direct contact with occluded or sorbed fuels.

The lack of apparent change in soil contaminants is significant. As indicated in the site characterization studies, by far the greatest mass of contamination is in the soils, not the groundwater. Therefore, site remediation is both temporary and incomplete without soil remediation.

### 3. Estimate of Removal

Because the sampling and analysis variability of the soils was too great to detect reduced JP-4 concentrations, the removal efficiencies can only be estimated by inference. Two mechanisms on the site have resulted in decreased hydrocarbons: volatilization and biodegradation.

#### a. Volatilization

Contaminants on the site had several opportunities to volatilize: in the aeration basin, in the untreated spray irrigation water, and directly from the soils.

##### (1) Aeration Basin

As discussed previously, the aeration basin removed more than 90 percent of most volatiles, but a better estimate of total hydrocarbon removal can be made from the TOC removal analysis. Pilot testing indicated that TOC was reduced on the average by approximately 20 mg/L in the aeration basin. Of the 21.4 million gallons pumped in the course of the investigation, approximately 20.4 million gallons were treated in the aeration basin. From this can be estimated that approximately 3,400 pounds of hydrocarbons were removed by this aeration basin.

##### (2) Untreated Spray Irrigation

Approximately 1 million gallons of unaerated groundwater were spray irrigated. Testing indicated that the volatile removal efficiency of the spray system was similar to that of the aeration basin. Assuming that similar TOC removal was also achieved, it can be estimated that an additional 170 pounds of hydrocarbons were volatilized from this spray.

##### (3) Direct Volatilization from the Soils

The direct volatilization of JP-4 hydrocarbons to the atmosphere at the Eglin POL Demonstration site may be estimated by the application of a simple model.

JP-4 is a light middle distillate (65 percent gasoline, 35 percent light petroleum distillate) with an average boiling range point of 176 to 287 C (as would be expected of an aged fuel, the 1984 Weston report found the Eglin fuel to have a somewhat higher boiling point than is typical for JP-4). Benzene, with a boiling point of 80.1 C, a vapor pressure of 76 mm Hg at 20 C, and a molecular weight of 78 g/mole (Reference 30) can be used to illustrate the

magnitude of volatilization in the course of this investigation. Using Shen's (Reference 31) model for vapor emissions from subsurface sources, the following equation may be applied:

$$dV_g/dt = D_i C_s (P_t)^{4/3} W_i (1/L) A$$

where

$V_g$  = volume of gas emitted

$t$  = time

$D_i$  = benzene diffusion coefficient

$C_s$  = equilibrium vapor concentration of the gas

$P_t$  = soil porosity

$W_i$  = weight fraction of contaminant in soil

$L$  = average depth to contamination.

The following values may be assumed for the Eglin site:

$D_i = 9.0 \times 10^{-6} \text{ m}^2/\text{sec}$

$C_s = 76 \text{ mm Hg}$

$P_t = 0.355$

$W_i = 5 \times 10^{-5}$  (5 percent of 1,000 mg/kg total petroleum hydrocarbon, a reasonable assumption for benzene concentration in field capacity saturated sandy solid)

$L = 3 \text{ ft}$

$A = 1.5 \text{ acres.}$

These assumptions yield an estimated benzene emission rate of 18 pounds per year. Over the project lifetime, 24 pounds of benzene would have been emitted. Because benzene is consistently more volatile than the average residual compound on site, it is reasonable to assume that no more than 50 pounds of hydrocarbons volatilized directly from the soil over the project's lifetime.

#### (4) Volatilization Estimate

The following is the estimate of volatilization from the site over the lifetime of the project:

Aeration Basin	3,400 pounds
Spray Irrigation	170 pounds
Direct Volatilization	50 pounds
<b>TOTAL</b>	<b>3,600 pounds</b>

#### b. Biodegradation

Although oxygen delivery never approached design levels, the oxygen delivered to the groundwater does appear to have been consumed, and most of it probably served to degrade and oxidize JP-4 hydrocarbons. It has been estimated (Section IV.B) that 16 percent of the hydrogen peroxide delivered was converted to oxygen that was used for biodegradation. As stated earlier, the approximately 94,000 pounds of 35 percent hydrogen peroxide was applied should have resulted in approximately 16,500 pounds of available oxygen. Assuming that 16 percent of this was used, and assuming that three pounds of oxygen oxidized one pound of hydrocarbon, it can be reasonably

estimated that approximately 900 pounds of hydrocarbons were biodegraded by oxygen from the hydrogen peroxide. In addition, it can be assumed that the 8 mg/L of oxygen from the aerator was also used for biodegradation. This would have biodegraded an additional 500 pounds of hydrocarbon. Therefore an estimated 1,400 pounds of JP-4 hydrocarbons were biodegraded.

c. Removal Estimate

Based on the preceding discussion, the following total removal was estimated:

Volatilization	3,600 pounds
Biodegradation	1,400 pounds
 TOTAL	 5,000 pounds

Assuming, as previously discussed, that the site originally contained 16,500 pounds of hydrocarbons, it is estimated that 30 percent of this hydrocarbon was removed. This estimated removal is very likely too small a fraction of the total, given sampling and analytical variability, to observe a reduction in hydrocarbon concentrations over time. This supports and appears to explain the lack of obvious pattern to all soil data and some groundwater hydrocarbon data.

## SECTION V

### CONCLUSIONS

#### A. TECHNOLOGY ASSESSMENT

Although numerous laboratory studies have proven the scientific principles of enhanced biodegradation, the Eglin AFB field test demonstrated that the implementation of a full-scale biodegradation system at a relatively simple site could encounter serious engineering limitations. The success of this technology depends on the uniform contact of oxygen, microorganisms, and contaminants. Intense sampling at the Eglin AFB test site indicated that this contact was not achieved, despite the use of three application methods and very permeable soils. This failure was particularly evident in the unsaturated zone of the spray application area, where 190 pore volumes of oxygen and nutrient-enriched water had no noticeable impact on soil contaminant levels. While groundwater contamination on the site generally decreased, other removal mechanisms, such as volatilization of contaminants in the above-ground aeration basin and dilution, contributed significantly to this reduction. Two observations are of great importance to others contemplating the use of this technology: peroxide instability and poor water/fuel contact.

The instability of hydrogen peroxide in the Eglin AFB soils greatly reduced oxygen transfer throughout the treatment zone and resulted in wasteful offgassing. Despite numerous attempts to improve peroxide stability, the lack of peroxide transport beyond the point of injection greatly reduced the potential for biodegradation.

Even when 190 pore volumes of oxygen-saturated water and nutrients were introduced to the unsaturated soils in the spray application area, no significant removal of contaminants was measured. Soil column research has shown that below a certain threshold level, fuel hydrocarbons may be trapped in microscopic soil pores and inaccessible to water passing through the larger pores (Reference 32). In this case, years of washing and biological enhancements will do little to accelerate the release and biodegradation of contaminants in these micropores. While fuel inaccessibility has its greatest impact on the treatment of the unsaturated zone, it will also limit the removal of fuel components from the saturated zone at low-ppb levels.

#### B. COST ASSESSMENT

The original intent of this project was to demonstrate a complete site remediation. Based on this objective, a cost model might have been developed for application at other sites. Due to the incomplete nature of the site remediation and hydrogen peroxide delivery problems, it cannot be firmly concluded with any degree of confidence that the in-situ enhanced biodegradation technology applied here could successfully remediate a site's hydrocarbon contamination to low mg/kg levels in soil and low ug/L levels in groundwater. Some general conclusions as to cost and some development of unit costs which may be transferable to other sites, however, is possible.

# 1. Eglin Site Specific Costs

The following is a speculative estimate for total site remediation cost at the Eglin POL Site, based on the following assumptions:

- Total hydrocarbon contamination: 16,500 pounds
- Capital construction costs:

Recovery well construction and pump installation	\$ 50,000
Injection system installation	40,000
Aeration/iron removal system total capital	5,000

Total Capital Cost \$ 95,000

- Annual operating costs:

Electric power	\$ 2,500
Peroxide injection equipment rental	18,000
Nutrient injection equipment rental	6,000
Full time site operator	40,000
Supervision	20,000
General maintenance and minor equipment replacement	20,000
Sampling and chemical analysis	25,000
Hydrogen peroxide (100 mg/L @ 30 gpm)	
4,500 gallons of 35% @ 4.20/gallon	19,000
Nutrients 5,000 lbs @ 0.5/pound	2,500

Total Annual Operating Costs \$153,000

- Treatment period 10 years, at the following removal rates (pounds):

	Year				
	1	2	3	4	5
Volatilization	2,400	1,200	850	650	450
Biodegradation	1,000	1,000	1,000	1,000	1,000

	Year				
	6	7	8	9	10
Volatilization	300	250	200	150	100
Biodegradation	1,000	1,000	1,000	1,000	1,000

Total 16,500 pounds

- The initial equipment purchased with the capital investment will last 5-6 years and be replaced once during the 12 year lifetime

Based on these assumptions the total cost estimate would be:

Capital cost 95,000 x 2	\$ 190,000
Annual operating cost 153,000 x 10	1,530,000
Total Cost	\$1,720,000

For those wishing to apply this estimate to other sites, several things must be considered:

- The Eglin site had very shallow groundwater and was easily accessible, yet secure, resulting in lower capital costs than most sites.
- These costs assume full cleanup is possible, which may not be the case.
- The aeration system did not allow any cost for offgas or air treatment.
- No costs are included for initial site characterization, free-product recovery, regulatory interface or permitting, or reporting.
- The iron problem would most likely require additional treatment costs, not included here.
- These costs include no process engineering; that is, no bench-scale testing, no site-specific design--it is assumed that the design as described in this report is implemented.

## 2. Unit Costs

The following generalizations on unit costs specific to in-situ enhanced bioreclamation are possible:

- Oxygen is typically limiting, the most costly chemical, and the major key both to success and cost. Available oxygen sources and their unit costs are as follows:

	Cost per pound	Solubility limit
Hydrogen peroxide	\$1.50-2.40	fully miscible
Pure oxygen	\$0.05-0.10	40± mg/L
Air	0	8± mg/L

The costs per pound are for available oxygen. They are chemical costs only, and do not include the delivery system costs.

- Nutrients are generally of secondary consideration from a chemical cost standpoint. For this project, total hydrogen peroxide costs were approximately \$40,000 for the chemical and \$27,000 for rental of the special storage and injection equipment. The total nutrient costs were approximately \$4,000 for the chemicals and \$9,000 for rental of storage and injection systems. Despite the lower cost, it is important both to ensure that adequate nutrients are available for biodegradation and that the nutrient salts do not form insoluble precipitates which can block or clog injection systems and limit the effectiveness of transport. The assumption that nutrients are a minor cost consideration and therefore should be automatically introduced in excess must be avoided.

## SECTION VI

### RECOMMENDATIONS

Based on this investigation the following recommendations have been developed:

#### A. IMPROVED LABORATORY FEASIBILITY STUDIES

Improved laboratory bench-scale testing techniques are required. These should include:

1. Biodegradability testing to insure that the contaminant of concern can be biodegraded.
2. Bench-scale testing to predict in-situ biodegradation and oxygen use rates.
3. Bench-scale testing to permit determination of optimal but not excess nutrient dosing rates. At present most bench-scale microcosm testing appears to evaluate nutrient requirements during the microbial growth phase in a batch reactor. Optimal dosing rates for in-situ applications are assumed to be those which maximize growth in these batch microcosms. Typically, the in-situ application is a plug-flow situation (injection and withdrawal) in a porous medium. Microbial biomass does not appear to increase uniformly across the site for the project life, but rather most probably increases in the aerobic zones near the injection points. Over time, as these areas are remediated, the biomass should shift downstream to more-contaminated locations. This should result in an initial microbial biomass increase, which should then stabilize for the life of the project. The batch-growth-plus-microcosm approach to bench-scale studies currently in use does not appear to adequately address the real world plug-flow situation. Bench-scale tests should be adequately designed to ensure that determination of the in-situ limiting factor (nutrient or oxygen) is determined.
4. Bench-scale testing to predict geochemical interactions between the oxygenated nutrient-salt-laden injection water and site soils and groundwater. It is necessary to be able to predict nutrient transport efficiency accurately, any potential precipitation/plugging problems, and non-biological redox reactions which could result in oxygen demand.
5. Bench-scale testing which would accurately predict hydrogen peroxide stability and decomposition rates in-situ. Currently used laboratory testing does not appear to address this critical issue.

## B. FOCUS ON GROUNDWATER REMEDIATION

The insitu enhanced biodegradation technology as applied here is most effective in the saturated zone. The only application technique tested here which introduced treated water into the vadose zone was spray irrigation, and despite the passage of 190 pore volumes of treated water through that zone no observable effect of treatment was noted. The other injection methods, injection wells and galleries, appeared to have little or no ability to provide treated water contact to the vadose zone. In addition, the approach of using water as a carrier of oxygen in unsaturated soil appears financially unsound. Water is denser and more viscous than air, and therefore the cost of pumping it through soil is much higher than for air. And at \$1.50 to \$2.40 per pound, oxygen in hydrogen peroxide is substantially more expensive than in pure oxygen gas or air. It is recommended that this technology only be considered for remediation of saturated zones where either no unsaturated contamination exists or the source of groundwater contaminated has been remediated by other means.

## C. IMPROVED OXYGEN DELIVERY

In order to stimulate aerobic biodegradation, some form of oxygen delivery system is necessary. As pointed out by this study, hydrogen peroxide that is injected at widely separated points or spray irrigated has serious limitations. The difficulty with other oxygen sources, such as air or pure oxygen, is the solubility limitation. Pure oxygen does have the potential to increase available oxygen to 40± mg/L, but safety issues associated with pure oxygen storage on a POL site must be considered. After selection of an oxygen source, the delivery system design must be realistic to ensure adequate oxygen delivery to the entire contaminated site. A system such as the one used here was only capable of effectively delivering oxygen approximately one foot from the injection point. An adequate delivery system design would have placed injection and withdrawal points every one foot, not a realistic design.

Alternatives to hydrogen peroxide, pure oxygen, and air should be investigated. These could include in situ oxygen generation, gaseous oxygen transport as aprons, or other approaches. Alternative electron acceptors such as nitrates should also be investigated.

## D. MANDATORY ON-SITE PILOT TESTING

Because of the inability of controlled laboratory experiments to accurately predict many field engineering problems, anyone considering in situ enhanced biodegradation should conduct on-site pilot tests prior to committing to a full-scale remediation. The pilot test should closely resemble the full scale system and include an oxygen and nutrient application point, several soil and groundwater monitoring locations, and a simple withdrawal system to control the gradient. If hydrogen peroxide is to be used, the stability and transport of  $H_2O_2$  should be tested in situ. The impact of nutrient additions on permeability and potential iron or manganese oxidation problems should also be identified. A simple pump test should also be completed to ensure that adequate water can be recovered for use in oxygen transport. A checklist for conducting a comprehensive pilot test is provided in Appendix G.

#### E. IMPROVED FIELD SAMPLING TO ESTIMATE BIODEGRADATION

Even when the obstacles to performing enhanced biodegradation have been overcome, one challenge still remains: how to accurately measure the extent of biodegradation that has occurred in the heterogeneous subsurface. Improved methods of sampling and analysis are needed to document in situ biodegradation and account for other mechanisms of removal such as volatilization and dilution. We encourage other researchers to pursue this problem and to identify or develop several soil and groundwater analyses which, when used together, can provide a more quantitative determination of in situ biodegradation.

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APPENDIX A  
FIELD METHODS

## HYDROGEN PEROXIDE

Method                      Colorimetric

Principle                  Hydrogen Peroxide, under acid conditions, reacts with titanium sulfate to form a stable, intense yellow color complex.

Range                      0 - 50 ppm Hydrogen Peroxide

Interferences            None

### Equipment Provided -

1. Color Comparator (0 - 50 ppm scale)
2. Hydrogen Peroxide Reagent (50 ml)
3. Pipette, Dropping (1 ml)
4. Test Tubes (2) (10 ml)
5. Plastic Test Tube Stoppers (2)
6. Field Analytical Data Sheet (1 pkg.)

### Procedure -

1. Fill a 10 ml test tube to the mark with pre-filtered sample.
2. Add 1 ml of Hydrogen Peroxide Reagent to the sample, cap and mix. (Caution:  $H_2O_2$  Reagent contains concentrated sulfuric acid.)
3. Wait two (2) minutes for the yellow color to develop.

4. Insert the test tube into one of the two Color Comparater viewing slots.
5. Position the Color Comparater in front of a good light source and match the test sample with the color standard it most nearly resembles.
6. Read the Hydrogen Peroxide concentration (in ppm) directly. If the sample color lies between two standards, take the mid-point concentration as the correct sample reading.
7. If the Hydrogen Peroxide value is off-scale (greater than 50 ppm), dilute the sample 1:1 with demineralized water, and repeat steps 1 - 6  
Multiply the reading, in ppm, by 2 to obtain the correct value.
8. Discard the test solution. Rinse equipment with demineralized water.
9. Record H<sub>2</sub>O<sub>2</sub> results on Field Analytical Data Sheet provided.

o Multisample Test Procedures

When analyzing large numbers of well water samples, the following Multisample Test Procedure is recommended:

### Additional Equipment Provided

1. Sample Beakers, 50 ml (20)
2. Test Tube Rack, Polypropylene (1)
3. Test Tubes, 10 ml (20)

### -- Procedure

1. Using the 50 ml Sample Beakers provided, label one beaker for each well sample to be tested. Labeling should correspond to that entered into Field Sample Log Book.
2. Fill each beaker to the 50 ml mark with well sample.
3. If required, pre-filter any muddy or cloudy well samples as described elsewhere in this manual.
4. Using the pre-calibrated 10 ml Test Tubes provided, label one test tube for each well sample collected. Place the sample tubes in the white polypropylene rack.
5. Carefully fill each 10 ml Test Tube to the mark with the corresponding well water sample.
6. Add 1 ml of Hydrogen Peroxide Reagent to each of the labeled Test Tubes; cap and shake well to mix. Continue with the  $H_2O_2$  test as described in this Field Operations Manual.
7. Record  $H_2O_2$  results (in ppm) using the Field Analytical Data Sheets provided.

CHLORIDE  
LOW-LEVEL

Method Colorimetric - Titrimetric

Principle Chlorides, in neutral or slightly alkaline solutions, in the presence of potassium chromate, are precipitated by treatment with silver nitrate. A red to red-brown precipitate signals the chloride precipitation end-point.

Range 0 - 50 ppm chloride

Interferences- Other halides (bromides, iodides) and cyanide register as chlorides. Sulfide, sulfite and thiosulfate ions interfere but are readily eliminated by pretreatment with Hydrogen Peroxide. The end-point is pH sensitive. Sample pH must be between the ranges of 7 - 10 for best results.

Equipment Provided -

- |                                  |                 |
|----------------------------------|-----------------|
| 1. Hydrogen Peroxide Solution    | (10 ml)         |
| 2. Phenolphthalein Reagent       | (15 ml)         |
| 3. Sulfuric Acid Solution (0.5N) | (15 ml)         |
| 4. Chloride Reagent 1            | (15 ml)         |
| 5. Chloride Reagent 2B(1)        | (50 ml)         |
| 6. Test Tube, Measuring          | (10 ml) and Cap |
| 7. Direct Reading Titrator       | (0 - 50 units)  |

- (1) Footnote: Chloride Reagent 2B has a limited shelf life. Periodically, check against a known chloride standard. Discard chloride reagent 2B every six months.

8. Pipette, Plain Dropping
9. Sodium Hydroxide Solution (0.1N) (50 ml)
10. Wide Range pH Test Paper (2 - 10 pH)
11. Teflon<sup>R</sup> Titration Beaker (50 ml)
12. Field Analytical Data Sheet (1 pkg.)

Procedure -

1. Using a pre-filtered sample, fill the 10 ml Measuring Test Tube to the mark with the water to be tested.
2. If the sample is known to contain sulfide, sulfite or thiosulfate, add 5 drops of Hydrogen Peroxide to the test tube, mix well and wait one (1) minute.
3. Using a small piece of Wide-Range pH Test Paper (approximately 2 - 3 inch long strip), dip the test paper into the sample and determine sample pH using the accompanying color scale. If pH is between 7 - 10, proceed with step 4. If not, add 1 drop of Sodium Hydroxide (if pH is below 7.0) or 1 drop of Sulfuric Acid (if pH is above 10.0) and mix well. Recheck pH to assure 7 - 10 range.
4. Add 3 (three) drops of Chloride Reagent 1 to the sample in the test tube, seal with the Titration Tube Cap and gently swirl to mix. A clear yellow color will result. After color develops, pour sample into the white Teflon<sup>R</sup> Titration Beaker provided.
5. Fill the Direct Reading Titrator with Chloride Reagent 2B to the zero (0) "fill" mark as follows:

- a. Depress Titrator plunger to bottom (50 mark) to expel air.
- b. Remove screw-cap from Chloride Reagent 2B, exposing special perforated septum.
- c. Insert Titrator Tip into hole in septum firmly to assure tight, leak-proof seal.
- d. Invert Chloride 2B bottle, while holding Titrator. Be sure tip of Titrator is covered with liquid.
- e. Slowly withdraw Titrator plunger, filling Titrator body. Stop when bottom (curved part) of Plunger Tip is even with "zero" (0) mark.
- f. Turn Bottle and Titrator up-right, carefully withdraw Titrator and recap Chloride Reagent 2B bottle. Wipe any excess Reagent off Titrator Tip.
- g. Hold the Titrator Body in one hand. Slowly depress Titrator Plunger with the other hand to dispense Reagent 2B dropwise into the sample in the Titration Beaker. Swirl by hand to mix reagents/sample during titration.

6. Titrate the test sample until a persistent red to red-brown hazy precipitate forms. Record the titrator plunger reading. (If plunger goes all the way to the bottom before the red endpoint is reached, refill and repeat the titration procedure adding the Total Titration Volume).
7. Each small mark (0 - 50) on the Titrator is equivalent to 1 ppm chloride, permitting direct reading of chloride from the Titrator.
8. Discard test solution, rinse equipment with demineralized water.
9. Record chloride results on Field Analytical Data Sheet provided.

o Multisample Test Procedures

When analyzing large numbers of well water samples, the following Multisample Test Procedure is recommended.

Additional Equipment Provided

1. Sample Beakers, 50 ml (20)
2. Test Tube Rack, Polypropylene (1)
3. Test Tubes, 10 ml (20)

## Procedure

1. Using the 50 ml Sample Beakers provided, label one beaker for each well sample to be tested. Labeling should correspond to that entered into the Field Sample Log Book.
2. Fill each beaker to the 50 ml mark with well sample.
3. If required, pre-filter any muddy or cloudy well samples as described elsewhere in this manual.
4. Using the pre-calibrated 10 ml Test Tubes provided, label one test tube for each well sample collected. Place the sample tubes in the white polypropylene rack.
5. Carefully fill each 10 ml Test Tube to the mark with the corresponding well water sample.
6. If the sample is known to contain sulfide, sulfite, or thiosulfate, add 5 drops of Hydrogen Peroxide to the Test Tube, cap, mix well, and wait one (1) minute.
7. Using a small piece of Wide-Range pH Test Paper (approximately 2-3 inch long strip), dip the Test Paper into the Test Tube sample and determine the sample pH (using the pH color scale). If pH is between 7 and 10, proceed with the test. If it is outside this range, treat as follows:

- (a) pH less than 7: Add Sodium Hydroxide dropwise, stir to mix. Continue until pH is between 7-10.
  - (b) pH more than 10: Add Sulfuric Acid dropwise, stir to mix. Continue until pH is between 7-10.
8. Add three (3) drops of Chloride Reagent 1 to the samples in each of the labeled Test Tubes. Cap, shake well to mix and place the Test Tubes back into the Polypropylene Test Tube Rack. A clear yellow color will form.
  9. After yellow color forms, pour each sample, in-turn, into the white Teflon\$STR\$SP Titration Beaker provided and proceed with the Chloride Test as described in this Field Operations Manual. Rinse the Titration Beaker with Deionized Water (1 time) between each test.
  10. Record Chloride results (in ppm) on Field Analytical Data Sheet provided.

## ORTHOPHOSPHATE

### LOW-LEVEL

Method - Colorimetric

Principle - Orthophosphates, in acidic solution, react with ammonium molybdate and potassium antimonyl tartrate to form phosphomolybdic acid. Treatment with ascorbic acid reduces this complex to an intense blue color.

Range - 0 - 6 ppm orthophosphate

Interferences - Low levels of arsenic ( 0.1 ppm) will measure as phosphate. Hexavalent chromium and nitrite may interfere slightly with color formation.

### Equipment Provided -

1. Color Comparator (0 - 6 ppm scale)
2. Phosphate Acid Reagent (50 ml)
3. Phosphate Reducing Reagent (5 gm)
4. Test Tubes (2) (10 ml)
5. Plastic Test Tube Stoppers (2)
6. Sulfuric Acid Solution (0.5N), 15 ml)
7. Measuring Spoon (0.1 gm)
8. Plastic Pipette (1 ml)
9. Demineralizer Wash Bottle (50 ml)
10. Wide Range pH Test Paper (2 - 12 pH)

Procedure -

1. Using a prefiltered sample, fill the 10 ml Test Tube to the mark. Check pH with Wide Range Test Paper to be sure sample is in neutral or acid pH range. Adjust, if needed, by adding 0.5N Sulfuric Acid Solution until pH is below 7.0.
2. Using the Plastic Pipette, add 1.0 ml of Phosphate Acid Reagent to the test sample in the Test Tube. Cap, using the orange stoppers provided and mix by shaking.
3. Using the 0.1 gm Measuring Spoon, add one (1) level spoon full of Phosphate Reducing Agent. Cap and shake well to dissolve.
4. Wait 5 minutes for blue color to develop (No Longer than 30 Minutes!)
5. Insert the Test Tube into one of the 2 viewing slots in the plastic Color Comparator.
6. Position the Color Comparator in front of a good light source and match the Test Sample with the standard it most nearly resembles.
7. Read the orthophosphate concentration (in ppm) directly. If the sample color lies between 2 standard colors, take the mid-point concentration as the correct sample reading.
8. If color is off-scale (too concentrated), make a 10 fold sample dilution as follows:

- a. Pipette 1 ml of sample into 10 ml Test Tube.
- b. Fill to 10 ml mark with water from Demineralized Wash Bottle.\* Cap and mix.
- c. Repeat steps 2 - 7.
- d. Multiply orthophosphate reading by 10 to obtain correct value in ppm.

9. Discard test solution. Rinse equipment with Demineralized Water.

## AMMONIA NITROGEN

### LOW-LEVEL

Method - Colorimetric

Principle - Ammonia, under alkaline conditions, reacts with mercuric iodide to form a yellow to yellow-orange color complex.

Range - 0 - 8 ppm ammonia

Interferences - Calcium, magnesium and iron will also react with alkaline mercuric iodide to form a precipitate. Pretreatment of the sample with sodium potassium tartrate (Rochelle's Salt) will minimize interferences.

### Equipment Provided -

1. Color Comparator (0 - 8 ppm scale)
2. Ammonia Nitrogen Reagent 1 (25 mls)
3. Ammonia Nitrogen Reagent 2 (25 mls)
4. Test Tubes (2) (5 ml)
5. Plastic Test Tube Stoppers (2)
6. Sodium Hydroxide Solution (0.1N) (50ml)
7. Pipette Dropping (1 ml)
8. Wide range pH Test Paper (2 - 10 pH)

Procedure -

1. Using a pre-filtered sample, fill a 5 ml Test Tube to the mark.
2. Add 4 drops of Ammonia Reagent No. 1 to the Test Tube, cap and mix.
3. Add 8 drops of Ammonia Reagent No. 2 to the Test Tube, cap and mix.
4. Wait 5 minutes for a yellow to yellow-orange color to develop\*.
5. Insert the Test Tube into one of the two Color Comparator viewing slots.
6. Position the Color Comparator in front of a good light source and match the test sample with the color standard it most nearly resembles.
7. Read the ammonia concentration (in ppm) directly. If the sample color lies between two standards, take the mid-point concentration as the correct sample reading.
8. If color is off-scale (too concentrated) make a 5-fold dilution as follows:
  - a. Pipette 1 ml of sample into 5 ml Test Tube.
  - b. Fill Test Tube to mark with demineralized water, cap and mix.
  - c. Repeat steps 1 - 7.
  - d. Multiply Ammonia reading by 5 to obtain correct value in ppm.
9. Discard test solution. Rinse equipment with demineralized water.

---

\* If color fails to develop, take test solution's pH with Wide Range pH Test Paper. If test solution pH is less than 10.0, add 1 - 2 drops 0.1N Sodium Hydroxide Solution, cap and mix. Wait 5 minutes and continue with step 5.

APPENDIX B  
SIEVE ANALYSIS

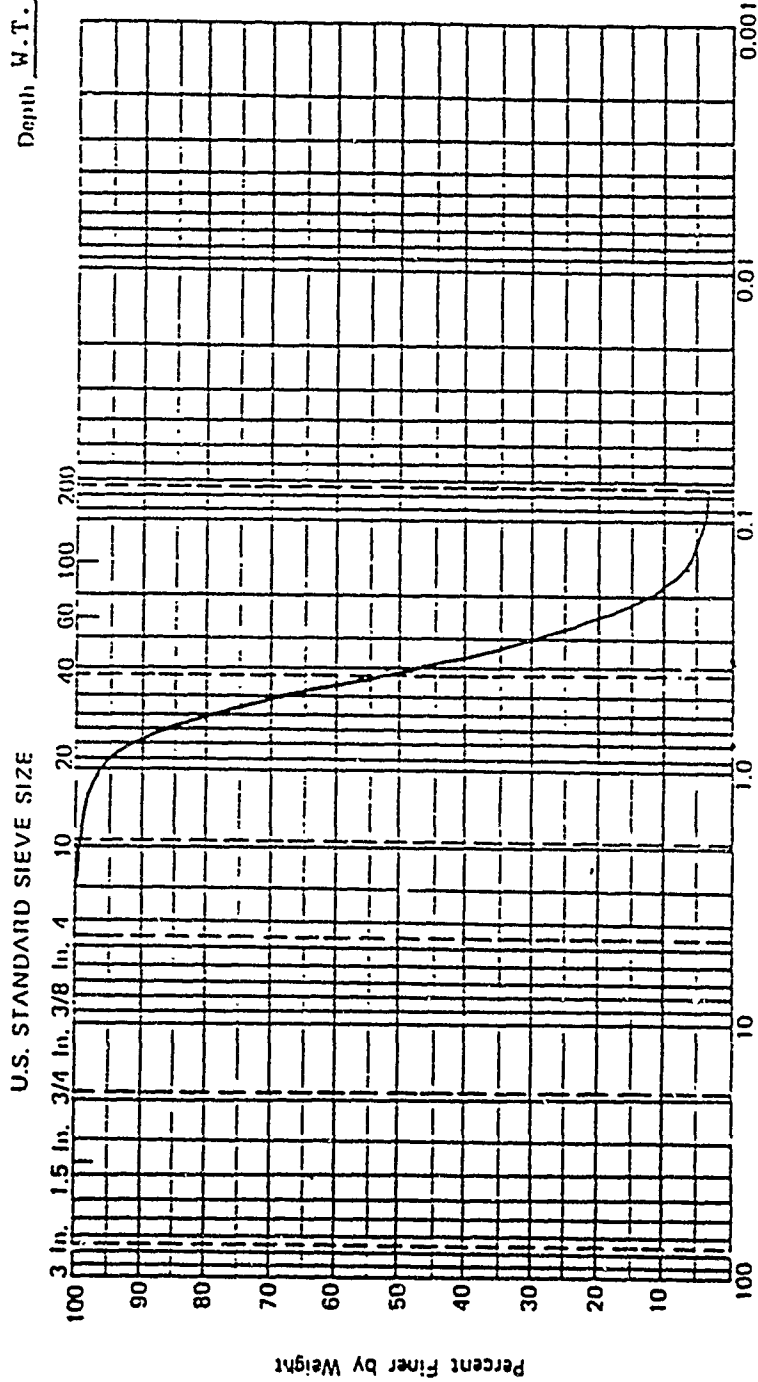
# GRAIN SIZE DISTRIBUTION AND LIQUID AND PLASTIC LIMIT DETERMINATIONS

Project DAF 71A

Boring No. EA-1 Sample No. 8380

2.5' below

Depth W.T. Elevation





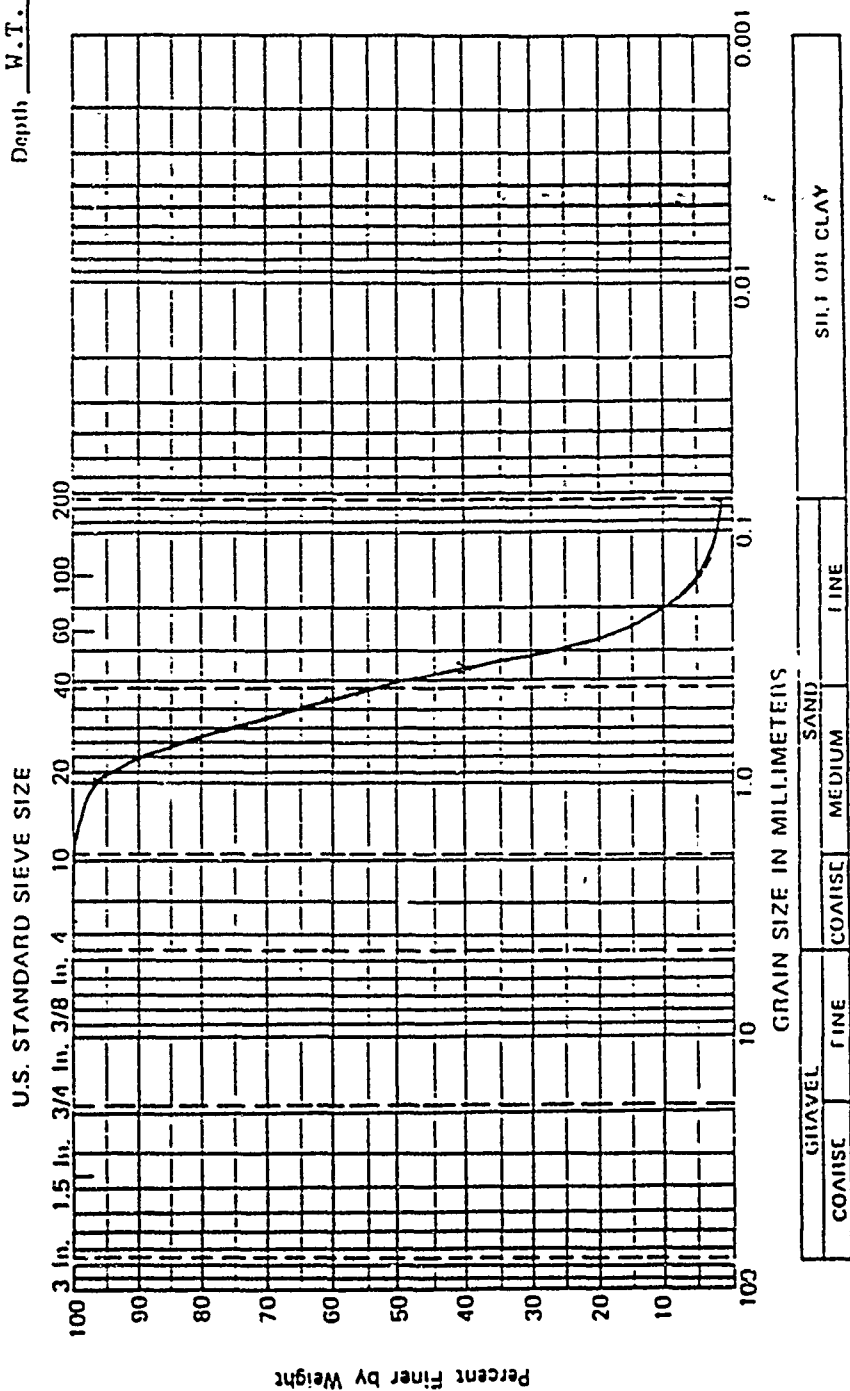
## GRAIN SIZE DISTRIBUTION AND LIQUID AND PLASTIC LIMIT DETERMINATIONS

Project DAF 71A

Boring No. EA-5 Sample No. 8390

2.0' below

Depth W.T. Elevation



GRAVEL	SAND		SILT OR CLAY
	COARSE	FINE	

CLASSIFICATION		NAT. WC	LL	PL	PI	REMARKS
SP	Poorly graded sand					



DAF 71A

DAF 71A

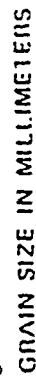
Boring No.	B	Sample No.	8320
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B

**Sample No.**

Depth W.T. 2.0' below Elevation

30



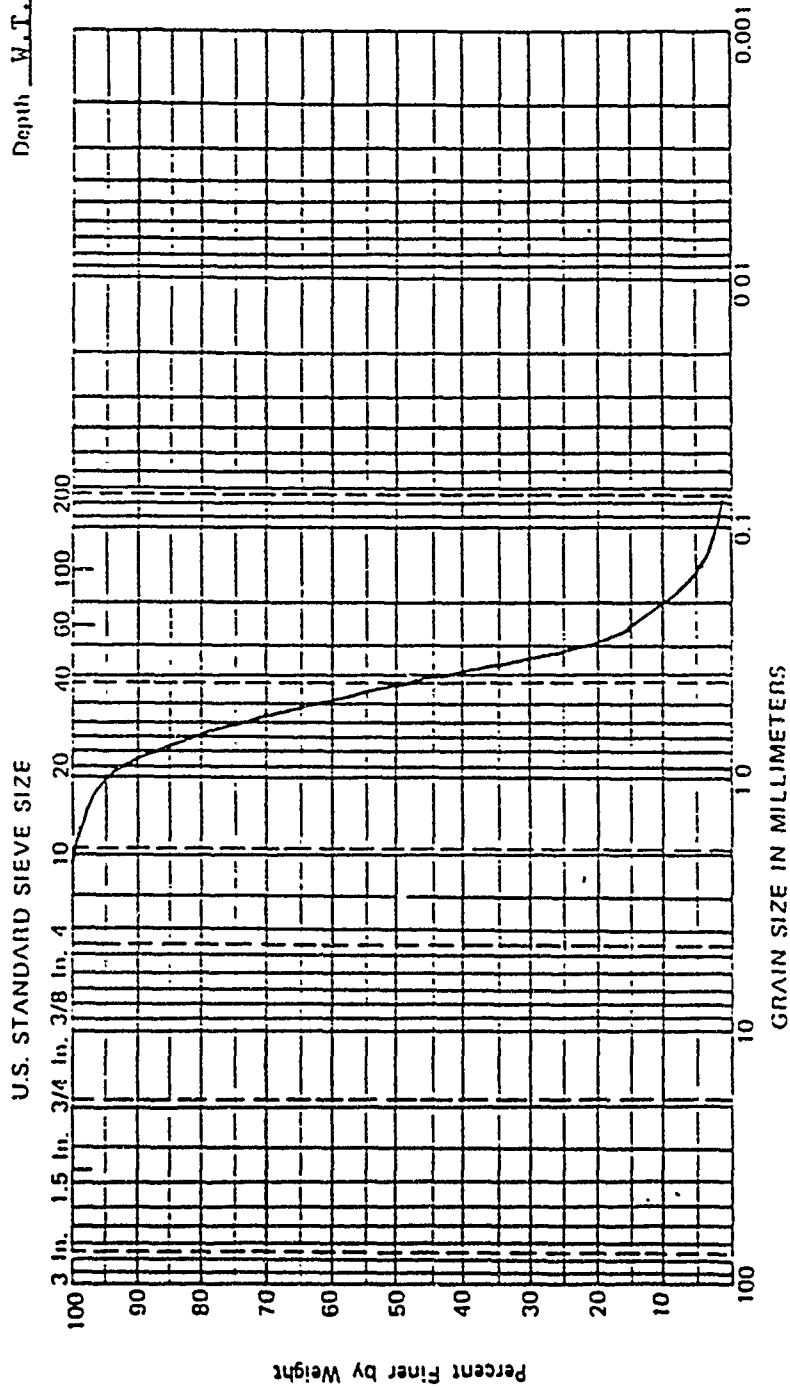
GRAIN SIZE IN MILLIMETERS									
GRAVEL		SAND				SILT OR CLAY			
COARSE		FINE		COARSE		FINE			
		CLASSIFICATION		NAT. WC		LL		PL	
Sp		Poorly graded sand						PI	
								REMARKS	

Project DAF 71A

Boring No. D Sample No. 8325

2.0' below

Depth W.T. Elevation           

[illegible]

APPENDIX C  
FREE PRODUCT RECOVERY

Operational Procedures for Preparing and  
Delivering Restore™ 375 Nutrient Solutions

A. Make-up Procedure

1. Inspect system to verify that batch tank T1 is empty, gear pump P1 is turned off, and all valves in process piping are closed.
2. Insert plunge rod into batch tank T1, 1-1/2" bottom outlet coupling.
3. Start with all valves closed.
4. Add required amount of water to batch make up tank T1. Maximum finished batch size should not exceed 300 to 350 gallons to prevent tank overflow and excessive splashing when mixer M1 is turned on and bags are dumped into tank.

Note: Water can be added directly to top of tank T1 via garden hose connected to potable water supply, or by using the self-priming Eco gear pump P1.

This is accomplished as follows:

- a. Connect hose from dilution water supply to 1" quick connect coupler which is screwed into valve V2.
  - b. Open valve V4 and then valve V2 slowly.
  - c. Start gear pump P1 by turning 3-way selector switch SS-1 to "hand" position and then pushing pump P1 start button. These controls are located on front of the control panel.
  - d. After desired amount of water has been added to tank T1, close valve V4, and disconnect dilution water supply hose.
5. Turn on mixer M1 by pushing mixer M1 start button located on front of control panel.
  6. Slowly dump required number of bags of Restore™ 375 into top of tank and allow mixing to continue until all the nutrient salts added have been completely dissolved. The mixer M1 can be turned off by pushing stop button M1.

B. Procedure to Adjust Pressure Relief Valve VR1

1. Fill 390-gallon batch tank T1 with approximately 300 gallons of potable water.
2. Start with all valves closed and plunge rod removed from bottom outlet of tank T1.
3. Adjust VR1 to high back pressure, (50 PSIG).
4. Open valves V1 and V4 for recirculation to tank.
5. Start pump P1 by turning three-way selector switch SS-1 to "hand" position and then pushing pump P1 start button. This should start recirculation to tank T1.
6. Slowly close V4 until pressure gauge PG-1 reads 45 psig.
7. Slowly adjust (turn out adjusting screw) VR1 until pressure gauge reads 40 psig. Some liquid should now be recirculating back to suction side of pump P1.
8. Slowly close V4 and observe pressure gauge. If pressure increases above 40 psig, slowly adjust (open) VR1 to reduce pressure back to 40 psig. Continue this procedure until V4 is completely closed and pressure gauge reads 40 psig. All the liquid being pumped is now being recirculated back to suction side of pump P1 and pump is now protected against mechanical damage. Maximum allowable pump discharge pressure is 50 psig.

AND SHEET PROTECTOR MY-11

C. Procedure to Regulate Flow Rate to Process Injection Point

1. Start with all valves closed.
2. Verify that pressure relief valve VR1 is adjusted properly. Procedure (B) should be followed or repeated to insure proper adjustment.
3. Connect one end of 1" flexible hose to 1" quick connect coupler attached to valve V3 and the other end to the process injection or use point.
4. Remove plunge rod from 1-1/2" bottom outlet of batch tank T1.
5. Open valve V1.
6. Turn three-way selector switch SS-1 to "hand" position and then push the P1 pump start button.
7. Observe and record liquid level in batch tank as shown by liquid level gauge LL-1. (There should be no liquid stream being discharged into batch tank). Observe pressure gauge PG1 and record (should be 40 psig +/-).
8. Slowly open valve V3 to the full open position and record the time. If back pressure of the system is greater than 40 +/- psig, there will be no recycle stream to tank. If the pressure gauge reading is less than that recorded in step 5, Restore™ 375 solution will be flowing to the process use point. The rate can be determined by timing the liquid level change in the batch tank. A 1" change of level = 12.1 US gallons.

Therefore, nutrient solution injection rate equals 12.1 gallons divided by the time, or -

$$\text{Rate (GPM)} = \frac{12.1 \text{ (Gals)}}{\text{Time (Minutes)}}$$

This will be the greatest rate possible.

9. The Restore™ 375 injection rate can be changed (reduced) by opening valve V4 to direct a portion of the pump discharge back to the batch tank. After each adjustment of valve V4, measure the rate of liquid level change (drop) in the batch tank.

10. If an injection rate is required lower than that obtainable in step (B-8), adjust valve V3 incrementally toward the closed position until the desired injection rate is obtained. Determine injection rate between each change.

WU SHEET PROJECTION MY-12

WU SHEET PROJECTION MY-12

D. Timed Interval Delivery of Restore™ 375 using Timer T1

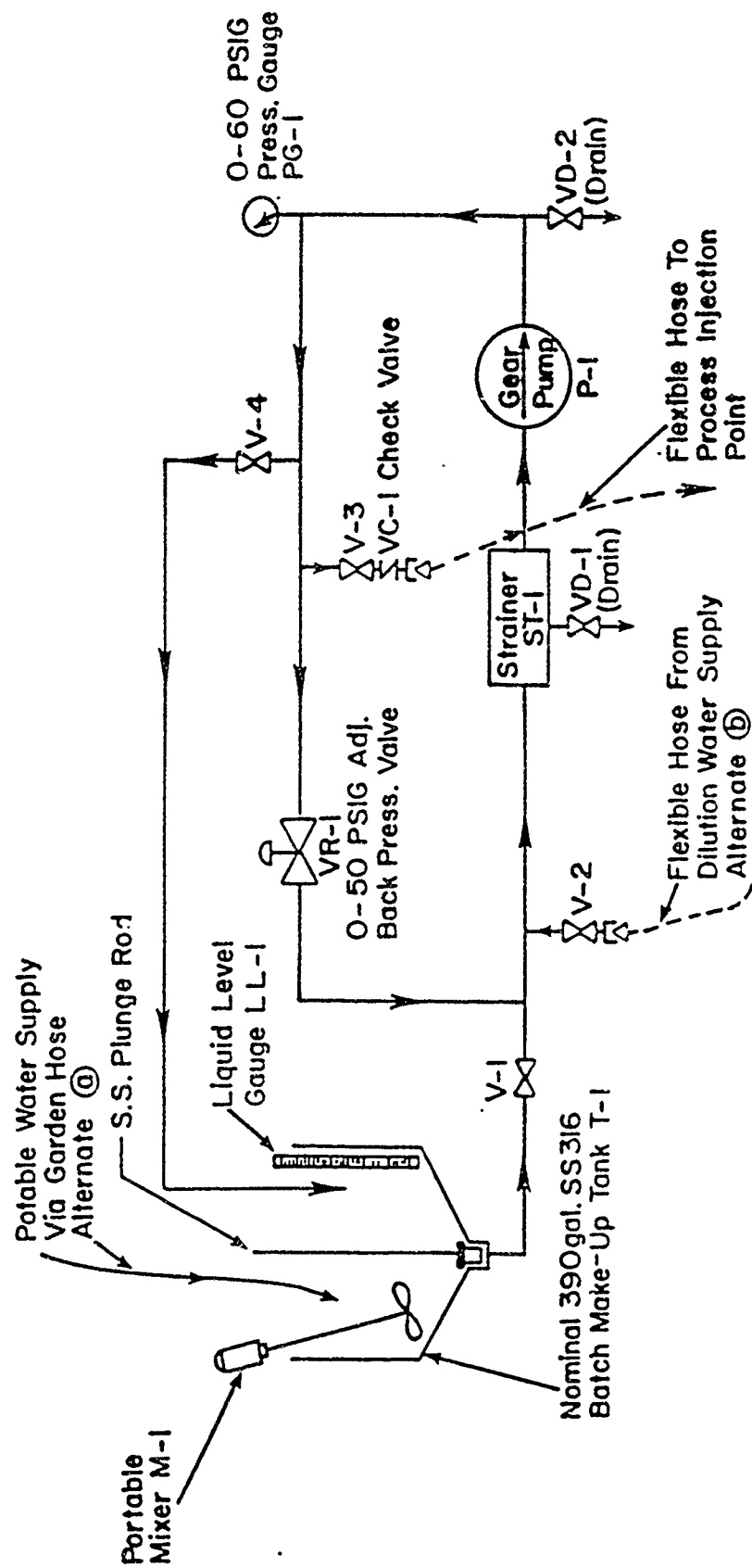
1. Set timer T1 to local time and set trippers to desired on-off operating schedule. Timer is located inside control panel.
2. Start with all valves closed.
3. Connect one end of 1" flexible hose to 1" quick connect coupler attached to valve V3 and the other end to the process injection point.
4. Remove plunge rod from 1-1/2" bottom outlet of batch tank T1.
5. Follow section (C) procedure to regulate flow rate to process injection and use point.
6. As soon as timer T1 has been programmed and the desired flow rate to process has been set, turn three-way selector switch SS-1 to "Auto" position. Timer T1 will automatically start and stop pump P1 as programmed.
7. Tank T1 should be periodically inspected to verify that Restore™ 375 is pumping to process use point.  
  
Note: The pump should not be run "dry" and should be stopped as soon as tank T1 is empty.
8. A fresh batch of Restore™ 375 solution can be made up at any time before the tank is empty by following Make-up procedure (A).

E. Shut Down Procedure for Restore™ 375 Nutrient System

If no further Restore™ 375 solution transfer is planned or required, or if ambient temperatures below the freezing point of the nutrient solution (normally a little less than 32°F) are expected, the piping system should be drained. This is an added protection against freezing and possible line/equipment damage even though the lines are heat traced and insulated. This can be done by disconnecting:

- a. 1" flexible hose connected to valve V3 quick connect coupler.
- b. Open strainer drain valve VD1.
- c. Open drain valve VD2.
- d. Open valves V4, V3, and V2 and remove dust plugs from 1" quick connect couplers.
- e. If batch tank T1 is empty, open valve V1 to drain any residual solution in 1" line from bottom of tank.

# Restore<sub>TM</sub> 375 Nutrient System Schematic Flowsheet



SK. NO. S-948-NI

Operational Procedures for Start-up of  
Restore™ 105/110 Storage Tank Metering System

A. Set-up

1. Insure all valves are closed.
2. Before opening any valves, pressurize Pulsatrol Pulsation Damper with 30 psi air.
3. See Diagram #1.
4. Open the main valve #1 to the storage tank.
5. Open valve #3 to the tank vent line.
6. Open valve(s) #4 to the Pulsafeeder Model 680 chemical feed pumps.
7. Open valve(s) #5 on the discharge side of the Pulsafeeder chemical feed pumps.
8. Connect 3/4 inch quick disconnect hose connection to female quick disconnect fitting on the discharge side of the Pulsafeeder pump line.
9. Connect female quick disconnect fitting on the opposite end of the hose to the injection fitting on the recycle groundwater line.

B. Electrical

Note: The control panel is wired so that in the event of an interruption in electrical power to the metering pumps, the system will not start up again until turned on manually with the On-Off switch. SS-1

1. Electrical power required to run the Pulsafeeder chemical metering pump is 110-120V AC and is supplied by inserting the female connection of a 12 or 14 gauge three prong extension cord into the receptacle on the bottom of the control panel.
2. Power is supplied to the Pulsafeeder chemical metering pump switches P-1, P-2, & P-3 by turning 3-way selector switch on the front of the control panel to "hand" position.

### C. Pump Calibration

1. The three Pulsafeeder Model 680 chemical metering pumps are rated at-

Pump #P-1	5.2 gph max
Pump #P-2	5.2 gph max
Pump #P-3	1.5 gph max

2. Turn all three pumps on by pressing green switches S-1, S-2, and S-3. This will insure that the feed lines from the storage tank through the metering pumps are filled with Restore 105/110 (hydrogen peroxide).
3. Turn pumps off by pressing red buttons S-1, S-2, and S-3.
4. Fill 500ml calibration cylinder above the 500ml mark with hydrogen peroxide by closing valve(s) #4 on the suction side of pump P-1 and opening valve #2 to the calibration tube.

Caution: Fill calibration tube slowly to prevent spilling over the top of the cylinder.

5. Close valve #2 to the calibration cylinder.
6. Open valve #4 on the suction side of P-1.
7. Shut off main valve #1 to storage tank.

Note: Pumping rate is established manually over a range of 0-100% of the pumps rated capacity by adjusting the micrometer adjusting knob on the back of the pump body.

At least three pumping rate measurements should be made:

1. 100% rated capacity
2. 50 or 60% rated capacity
3. 20 or 25% rated capacity

8. Turn power on to pump P-1.
9. Open valve #2 to calibration tube.
10. When liquid level reaches top line on calibration tube, begin timing flow rate.

11. At 30 seconds or (1) one minute shut off valve #2 on calibration tube record liquid level.
12. Turn off power to P-1.
13. Reduce pumping rate by turning micrometer knob on back of P-1 counter-clockwise to desired setting.
14. Refill calibration tube.
15. Repeat steps 5-12.
16. Reduce pumping rate on pump P-1 and follow the procedures described above.
17. When three measurements have been made, develop a graph to assist in determining pumping rates at different pump settings.
18. Repeat steps 4-12 to calibrate pumps P-2 and P-3.

D. Metering 105/110 to injection or process point

1. Open main valve #1 from tank.
2. Open appropriate valve(s) #4 on suction side of Pulsafeeder pumps.
3. Open appropriate valve(s) #5 on discharge side of Pulsafeeder pumps.
4. Turn on appropriate switch(s) S-1, S-2, or S-3 to energize pumps.
5. Adjust delivery rate by adjusting micrometer(s) knob(s) to appropriate % delivery.
6. Determine delivery rate using calibration procedure described in section E.

E. Calibration Curves

1. Diagram #2 shows a typical calibration curve for Pulsafeeder Model 680 metering pumps with a design capacity of 5.2 gph and are designated as P-1 and P-2 Diagram #1.
2. Diagram #3 is a typical calibration curve for Pulsafeeder Model 680 metering pumps with a design capacity of 1.5 gph and are designated as P-3 on Diagram #1.

Diagram No. 1

# Flow Diagram and Metering Pumps for 2500 Gallon Restore 105/110 (H<sub>2</sub>O<sub>2</sub>) Tank

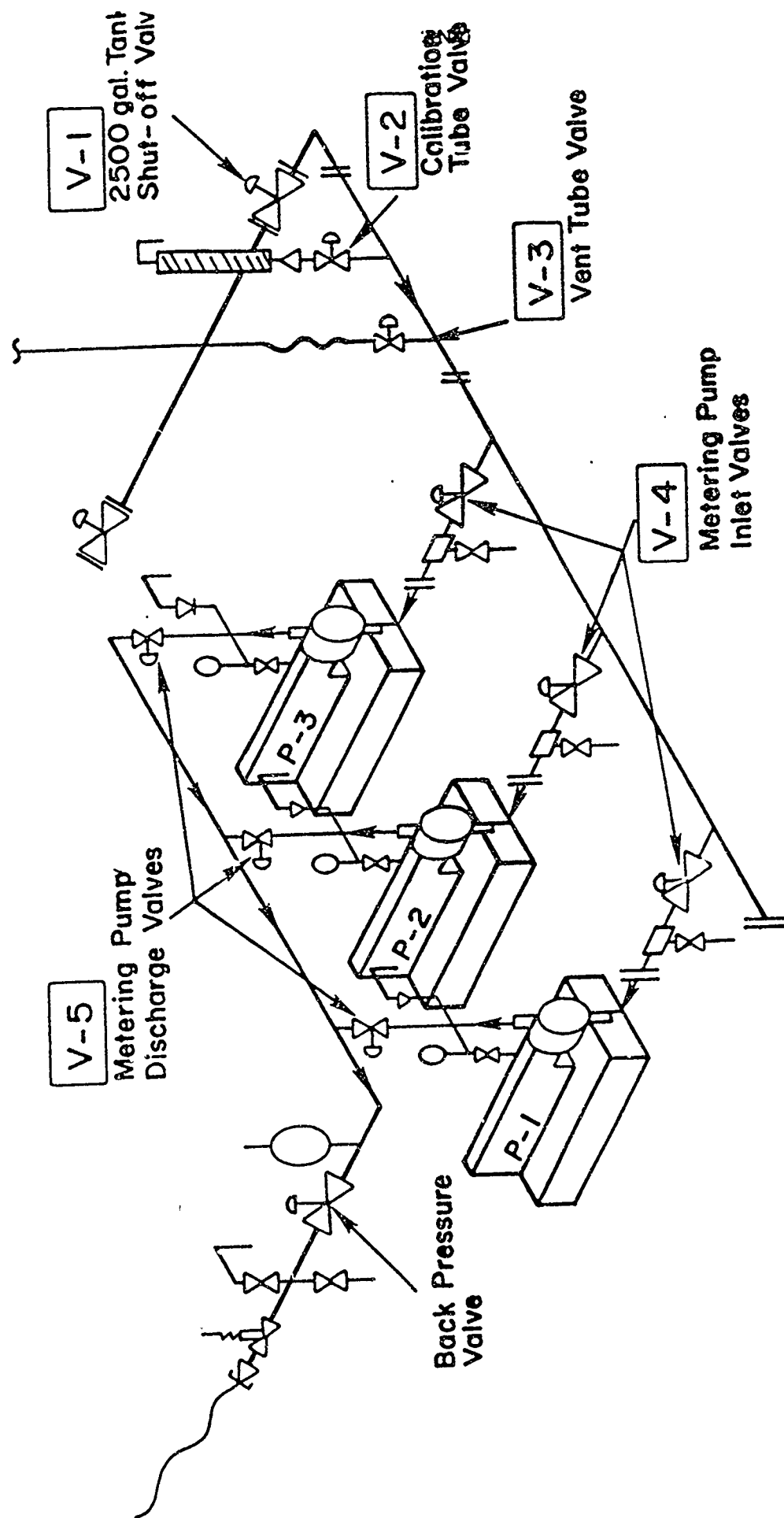
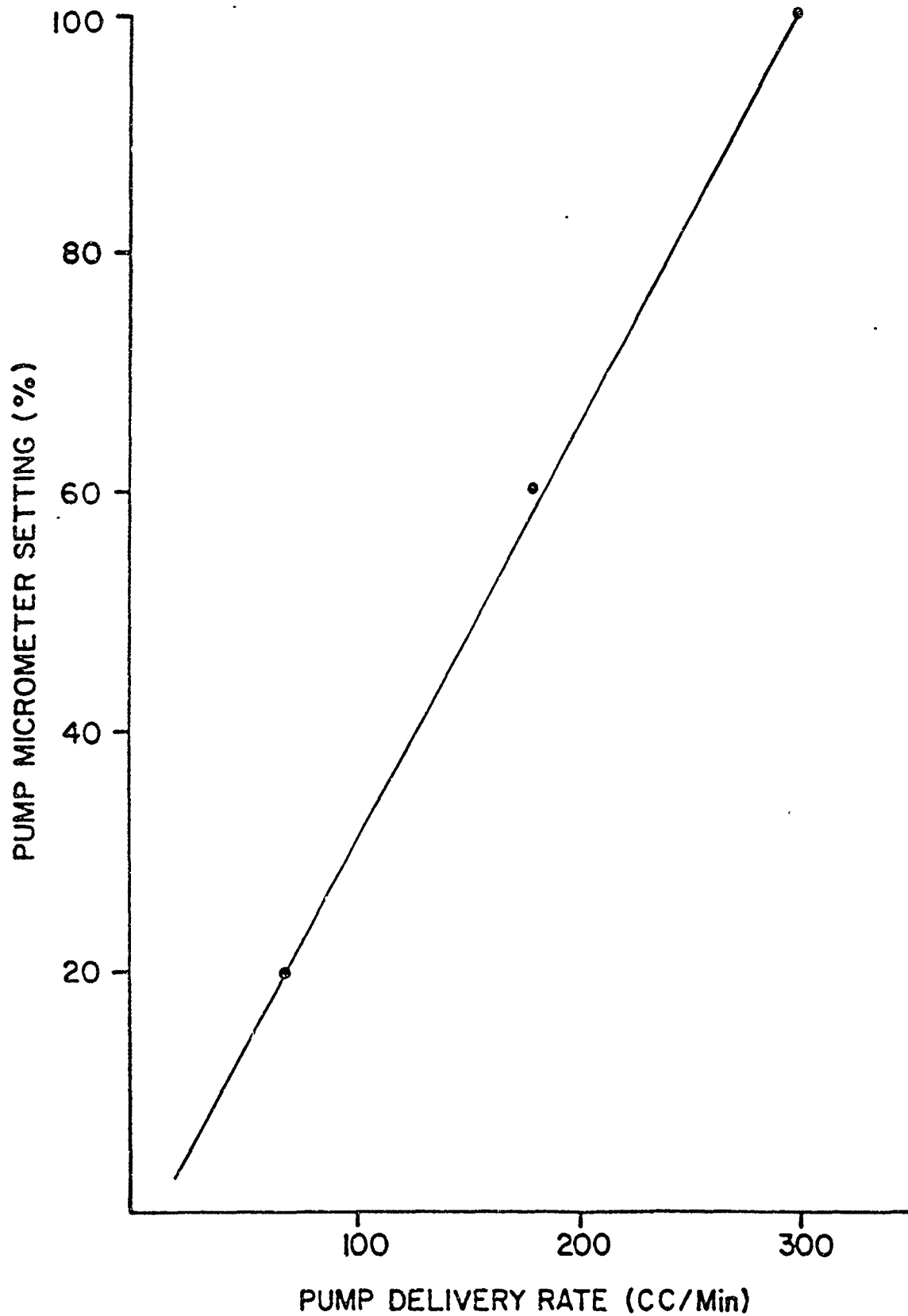


Diagram No.2



APPENDIX D  
HYDRAULIC HISTORY


MEMO FOR RECORD

FROM: HQ AFESC/RDVW (Mr Downey)

SUBJ: Increase in Free Product (JP-4) in Vicinity of RW-4

TO : Rob Hinchee  
Gaylen Brubaker/Mark Westray  
Kevin Slaughter

1. During the past few months, increased quantities of free product (JP-4) have been removed from RW-4 at our Eglin AFB research site. While these erratic movements of free product are not unusual, we were concerned that a new leak may have occurred in the JP-4 pipelines in the vicinity at RW-4.
2. On 1 December, a sample of this free product was taken from RW-4 and then analyzed with our GC/MS to determine the age of this fuel. The gas chromatographic result in Figure 1 was compared to a JP-4 chromatograph (Figure 2) from a sample taken in March from the center at the treatment area (EA-3)..
3. I have consulted with Dr. Mayfield, our in-house expert on JP-4 aging and GC/MS analysis of JP-4, and his opinion is that the RW-4 fuel is the same age as the March sample. A primary indicator of aged fuel is the lack of  $C_1-C_6$  compounds which are lost due to their high water solubility and volatilization. Figure 3 shows a chromatograph of a fresh JP-4 sample. Note the significant increase in peaks prior to 12 minutes in the fresh sample.
4. In summary, the free product at RW-4 appears to be the same age as samples taken at other locations on the site. While this increase in free product near RW-4 has upset our initial assumptions on remaining free product, it represents a very normal field condition that will be encountered at most bioremediation sites. If the quantity of free product recovered at RW-4 remains steady over the next three months we will re-evaluate its source and impact on the treatment area.



DOUGLAS C. DOWNEY, P.E.  
USAF Project Engineer

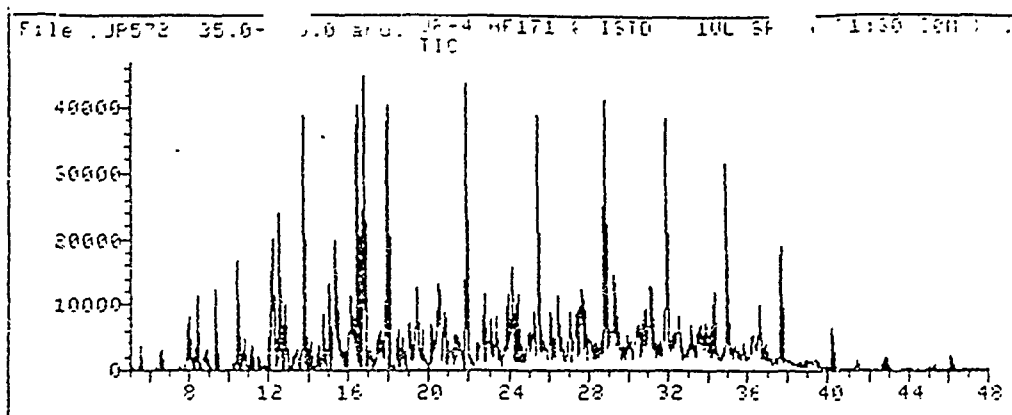


FIGURE 1. Fuel Sample from AW-4, 1 Dec 87

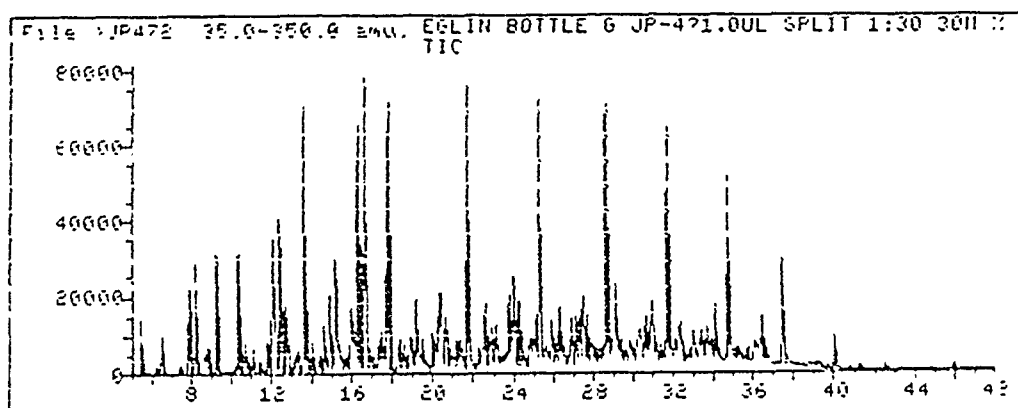


FIGURE 2. Fuel Sample from EA-3, 3 Mar 87

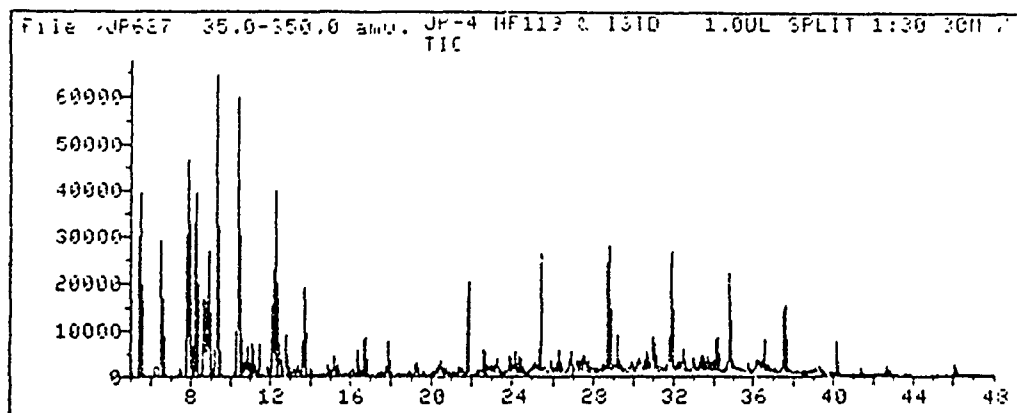
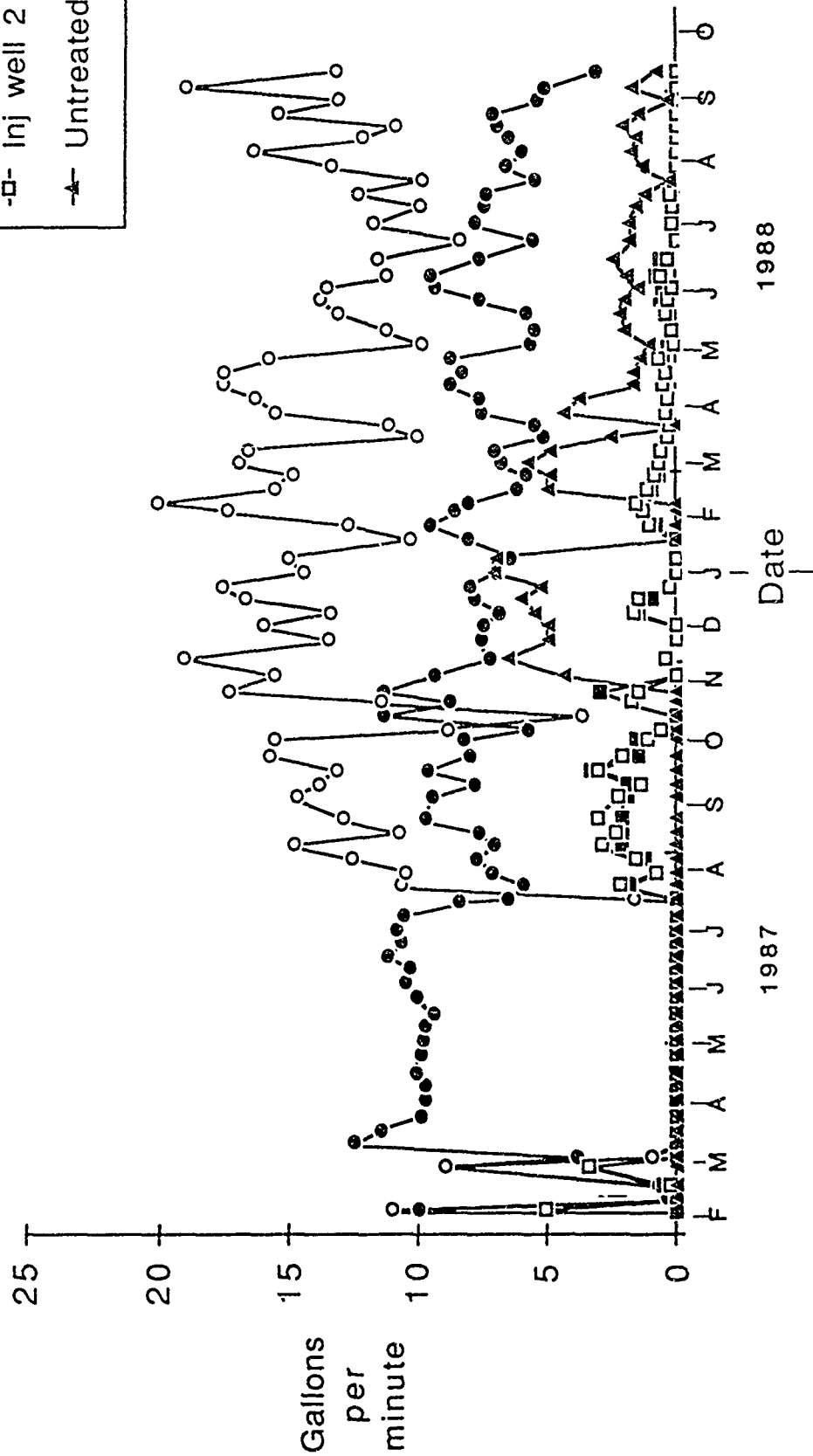
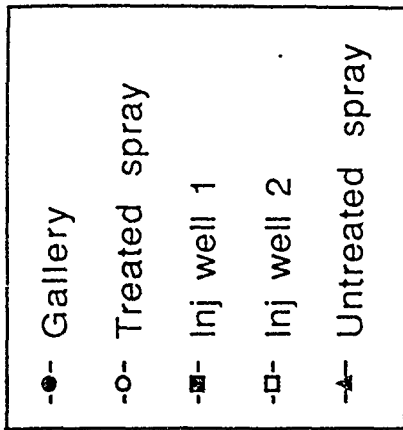


FIGURE 3. New Fuel Sample

APPENDIX E  
MISCELLANEOUS

# Injection System Pumping Rates



APPENDIX F  
PROJECT HISTORY

Project History, Eglin A.F.B. Proj # DAF71A

DAY	DATE	HISTORY
37	11/20/86	Initial soil vapor survey conducted
39	11/22/86	Initial quarterly soil and ground water sampling conducted
91	1/13/87	Auto Skimmer set up on site for free product recovery
105	1/27/87	Drillers started drilling injection and recovery wells
106	1/28/87	IT Corporations Peroxide and nutrient addition systems arrive on site
112	2/3/87	Ran initial pumping tests on recovery wells
119	2/10/87	Concrete basin broke while running pumping tests
126	2/17/87	Restarted system using a 1000 gallon settling basin
136	2/27/87	Started running three out of the four recovery wells thru sprinklers in an attempt to remove iron from the ground water
142	3/5/87	Turned on Peroxide addition to infiltration galleries at 100 ppm
148	3/11/87	Added three new infiltration galleries EGL5-EGL7
154	3/17/87	Turned up Peroxide addition rate to 200 ppm
160	3/23/87	First day of Carbonate/Bicarbonate addition to settling basin in an attempt to raise the pH of the ground water
163	3/26/87	Participated in periodic Air Force monitoring of wells on site
188	4/20/87	Installed monitoring well EA 22 in infiltration gallery trench for purpose of running Peroxide stability tests
199	5/1/87	Conducted first Peroxide stability test on site
203	5/5/87	Auto Skimmer is removed from site ending automatic free product recovery
213	5/15/87	First nutrient addition (Restore 375)
217	5/19/87	Started having trouble with Peroxide injection pumps vapor binding due to Peroxide decomposition, this continued for over a month until pumping rates were increased
252	6/23/87	Quarterly soil and ground water sampling conducted
273	7/14/87	Started using blowers and diffuser discs in pool for aeration of ground water
276	7/17/87	End of ground water treatment using sprinklers to decrease iron levels
293	8/3/87	First day of aeration and settling pool pretreatment of groundwater

296	8/6/87	Quarterly soil and ground water sampling conducted
297	8/7/87	Started Peroxide addition to all three systems at 100 ppm
304	8/14/87	Turned Peroxide addition rate to all three systems up to 200 ppm
314	8/24/87	Turned Peroxide addition rate to all three systems up to 300 ppm
316	8/26/87	End of Carbonate/Bicarbonate addition to aeration pool and beginning of Sodium Hydroxide addition to settling basin for pH adjustment
336	9/15/87	Installed new infiltration galleries GL8-GL11 in existing free product recovery trench EA 24 was installed in trench with new galleries for stability test purposes
350	9/29/87	Quarterly soil and ground water sampling conducted Tests run on aeration pool to test blower efficiency
353	10/2/87	Turned Peroxide addition rate to all three systems down to 100 ppm
370	10/19/87	Turned Peroxide addition rate to all three systems up to 300 ppm
379	10/28/87	Added two more spray heads to spray system on the up gradient side
384	11/2/87	Inj 1 and Inj 2 turned off due to low flow rates being achieved
386	11/4/87	Peroxide addition rate to infiltration galleries turned up to 4000 ppm for stability test
387	11/5/87	Peroxide addition is turned back on to infiltration galleries and spray application system at 300 ppm Untreated spray system started up at EA 8
391	11/9/87	Conducted SETAC tour of site
414	12/2/87	Turned on Inj 2 and added Peroxide at 500 ppm for stability test
422	12/10/87	Turned up Peroxide addition rate to infiltration galleries to 4000 ppm for stability test
428	12/16/87	Changed spray system over from impact type spray heads to mister type
449	1/6/88	Quarterly soil and ground water sampling conducted
472	1/29/88	Started using a three horse power blower in aeration system instead of two one horse power blowers
475	2/1/88	Added two more spray heads to spray system on the up gradient side
526	3/23/88	Quarterly soil and ground water sampling conducted Soil vapor is analyzed for % Oxygen, % Carbon Dioxide, % Hydrogen Sulfide, and % LEL Experimental galleries used for the first time
539	4/5/88	First Stability test run on experimental galleries

561	4/27/88	Vadose sampler installed in spray application area
668	8/12/88	Last day of sodium hydroxide addition
672	8/16/88	Last of the experimental galleries is turned off
679	8/23/88	Soil vapor is analyzed for % Oxygen, % Carbon Dioxide, % Hydrogen Sulfide, and % LEL
680	8/24/88	Quarterly soil sampling conducted
681	8/25/88	Last day of Peroxide addition to the site
684	8/28/88	IT Corporations Peroxide and nutrient addition systems are shipped off site
685	8/29/88	Quarterly ground water sampling conducted
706	9/19/88	Soil vapor survey conducted on site
707	9/20/88	Chloride transport test conducted on site
708	9/21/88	Soil vapor is analyzed for % Oxygen, % Carbon Dioxide, % Hydrogen Sulfide, and % LEL
710	9/23/88	Ran final pump test on recovery wells
745	10/28/88	All EA equipment is moved off site All Air Force equipment is picked up by Eglin personnel Conducted final walk thru of site with personnel from Eglin Air Force Base